The Role of Heterogeneous Chemistry in the Photochemical Oxidant Cycle: A Modeling and Laboratory Study

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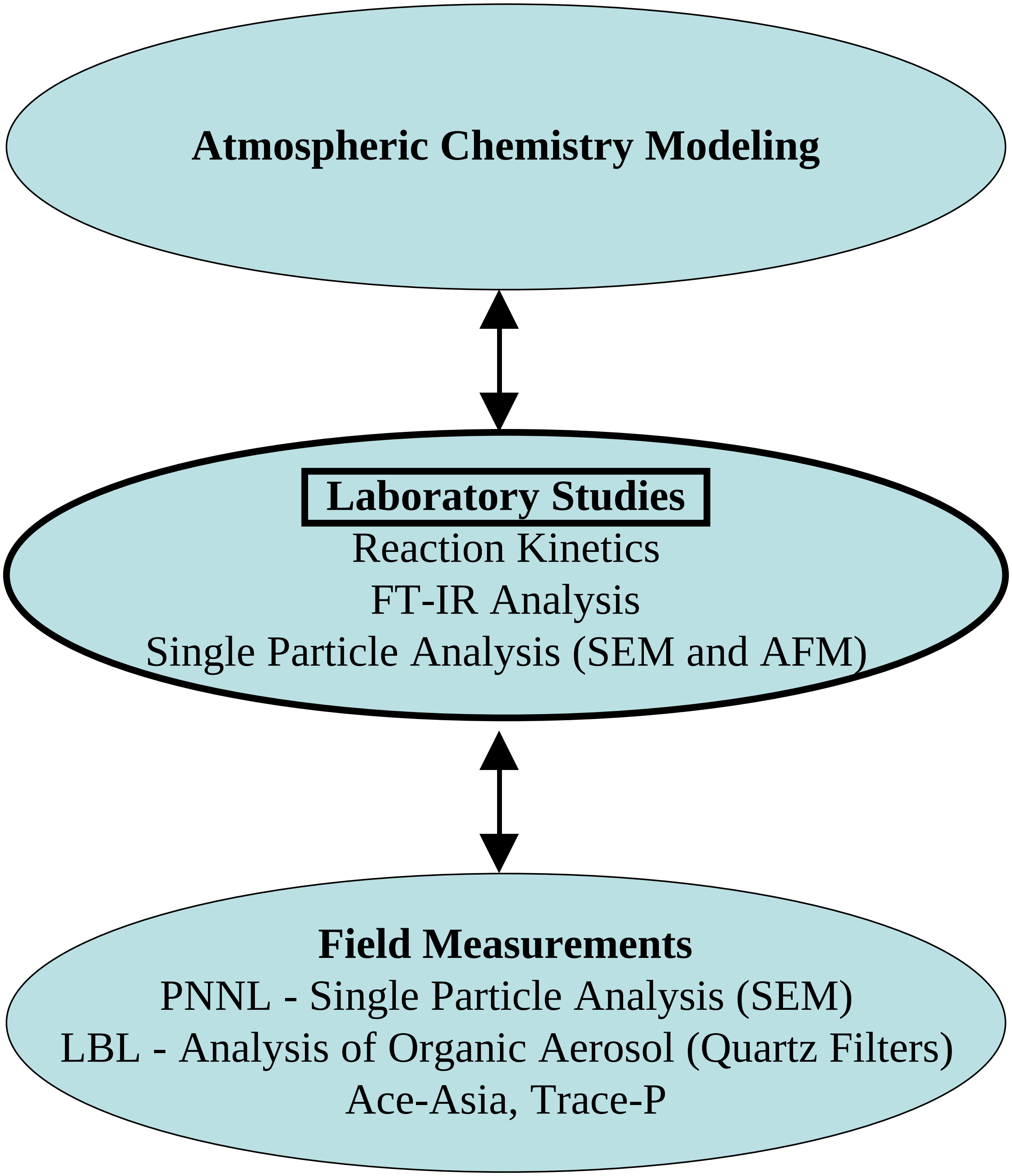

Atmospheric Chemistry Modeling
Laboratory Studies
Reaction Kinetics
FT-IR Analysis
Single Particle Analysis (SEM and AFM)
Field Measurements
PNNL - Single Particle Analysis (SEM)
LBL - Analysis of Organic Aerosol (Quartz Filters)
Ace-Asia, Trace-P

Laboratory Studies Designed to Aid In the Interpretation of Field Measurements of Atmospheric Particulates

Organic Aerosol
(Kirchstetter and Novakov - LBL)

quartz filter sampling artifacts can be related to the surface chemistry of quartz

e.g. surface reactions of alcohols and organic acids

$$SiOH + ROH \longrightarrow SiOR + H_2O$$
$$SiOH + ROOH \longrightarrow SiOOR + H_2O$$
$$ROOH \longrightarrow (ROOH)_2$$

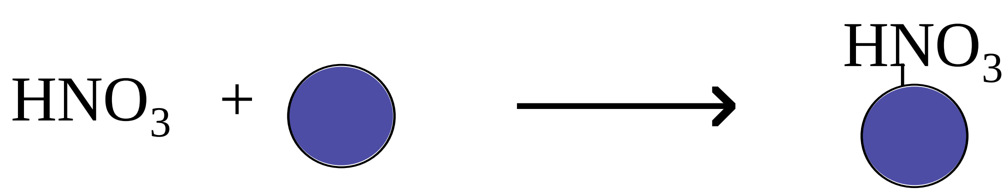
Atmospheric Chemical Processing of Aerosol
(Cowin and Laskin - PNNL)

Single particle analysis using SEM/EDX Analysis

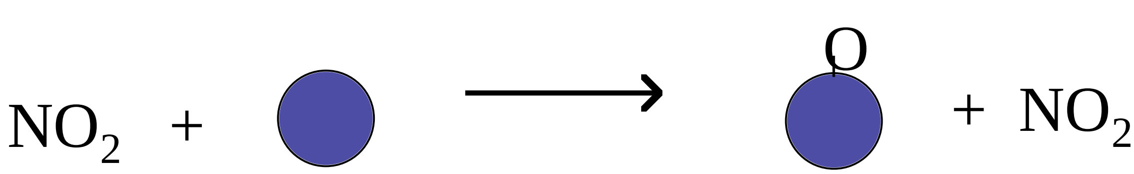
Chemical Role of Aerosol Particles in the Atmosphere

Can change the chemical balance of the atmosphere in two ways

Sink



Reactive Surface



$$H(a) + NO_2 \longrightarrow HONO$$

Heterogeneous Chemistry on Mineral Dust and Carbonaceous Aerosol

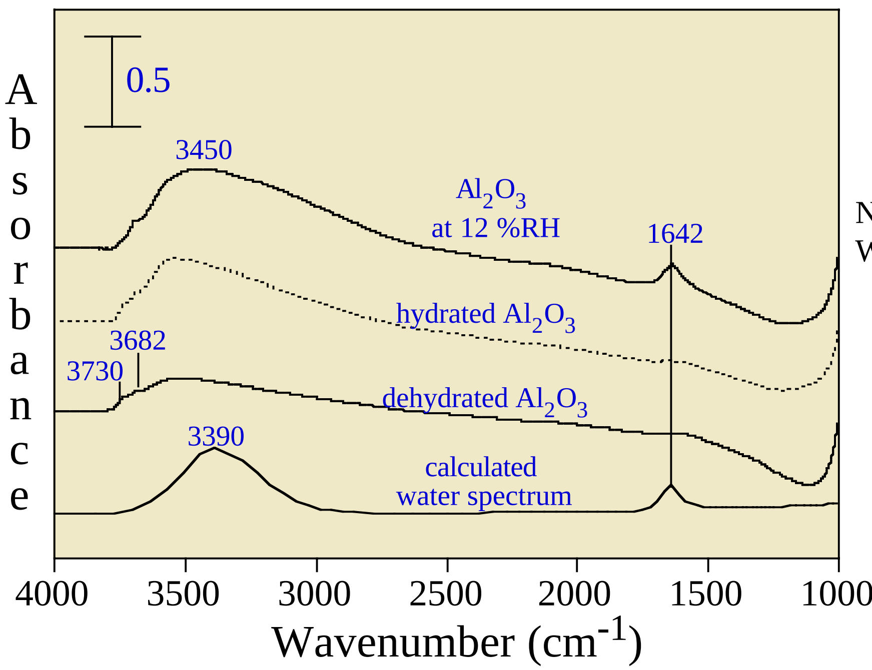
- Role of heterogeneous reactions in the photochemical oxidant cycle
- Trace atmospheric gases of interest include NO_2, **HNO_3**, **SO_2, O_3** and Organics (e.g. acetone, methanol, **acetic acid**…)
- Laboratory Models for Mineral dust
  - Oxides, carbonates, clays, aluminum silicates…

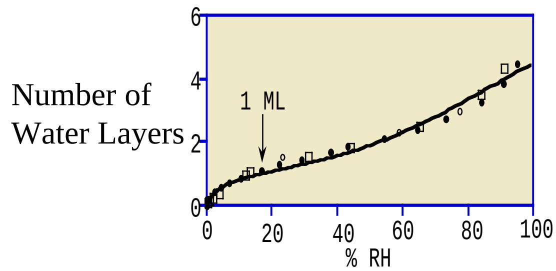
Single component oxides
SiO_2,
α-Fe_2O_3, α-Al_2O_3, TiO_2,
CaO, MgO,
Carbonates
$CaCO_3$
Dust samples
China Loess and Saharan Sand

Surface versus Bulk Compositions

Single Component Oxides

surfaces are truncated by hydroxyl group and adsorbed water



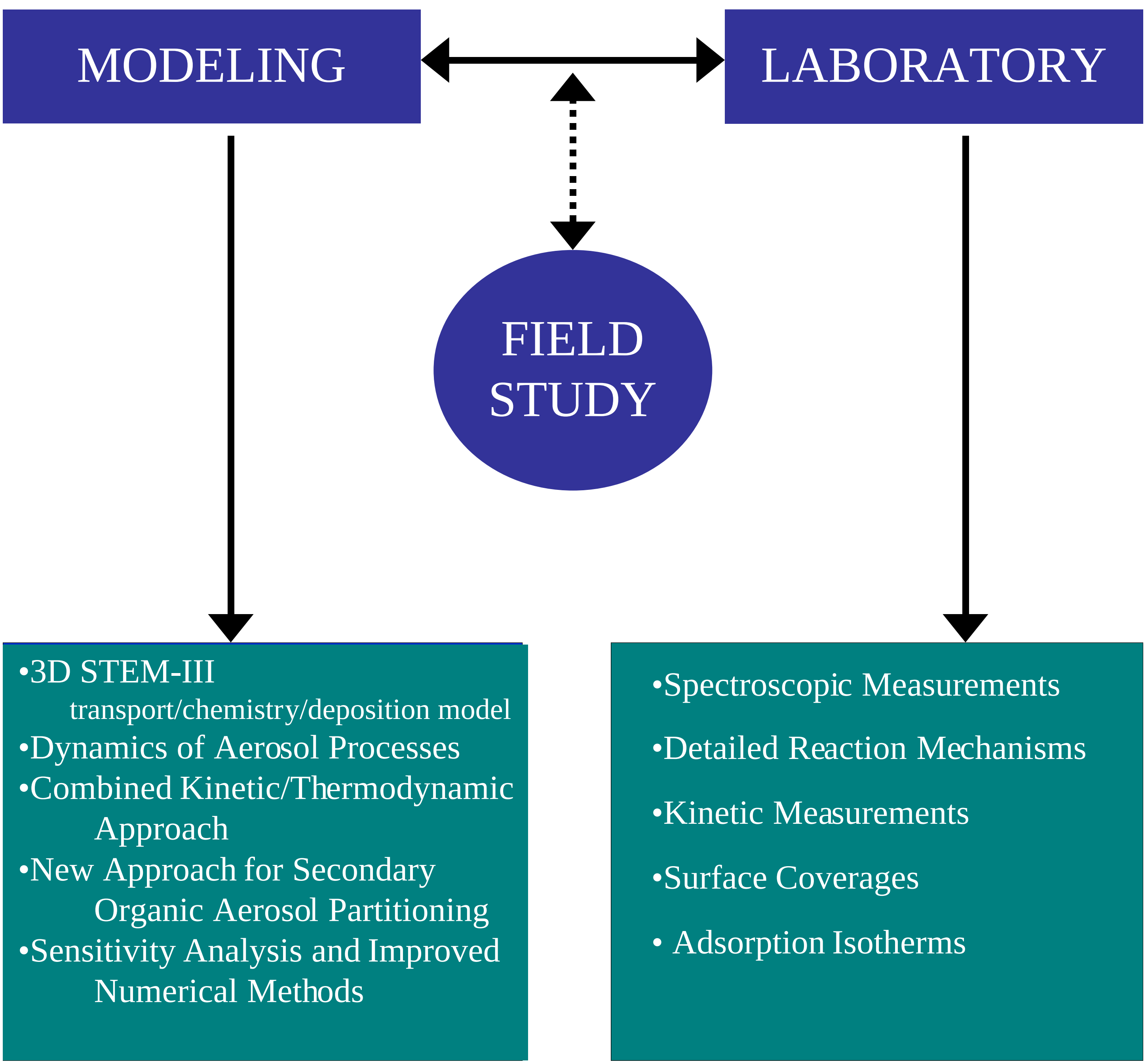


Basic oxides (e.g. MgO and CaO)

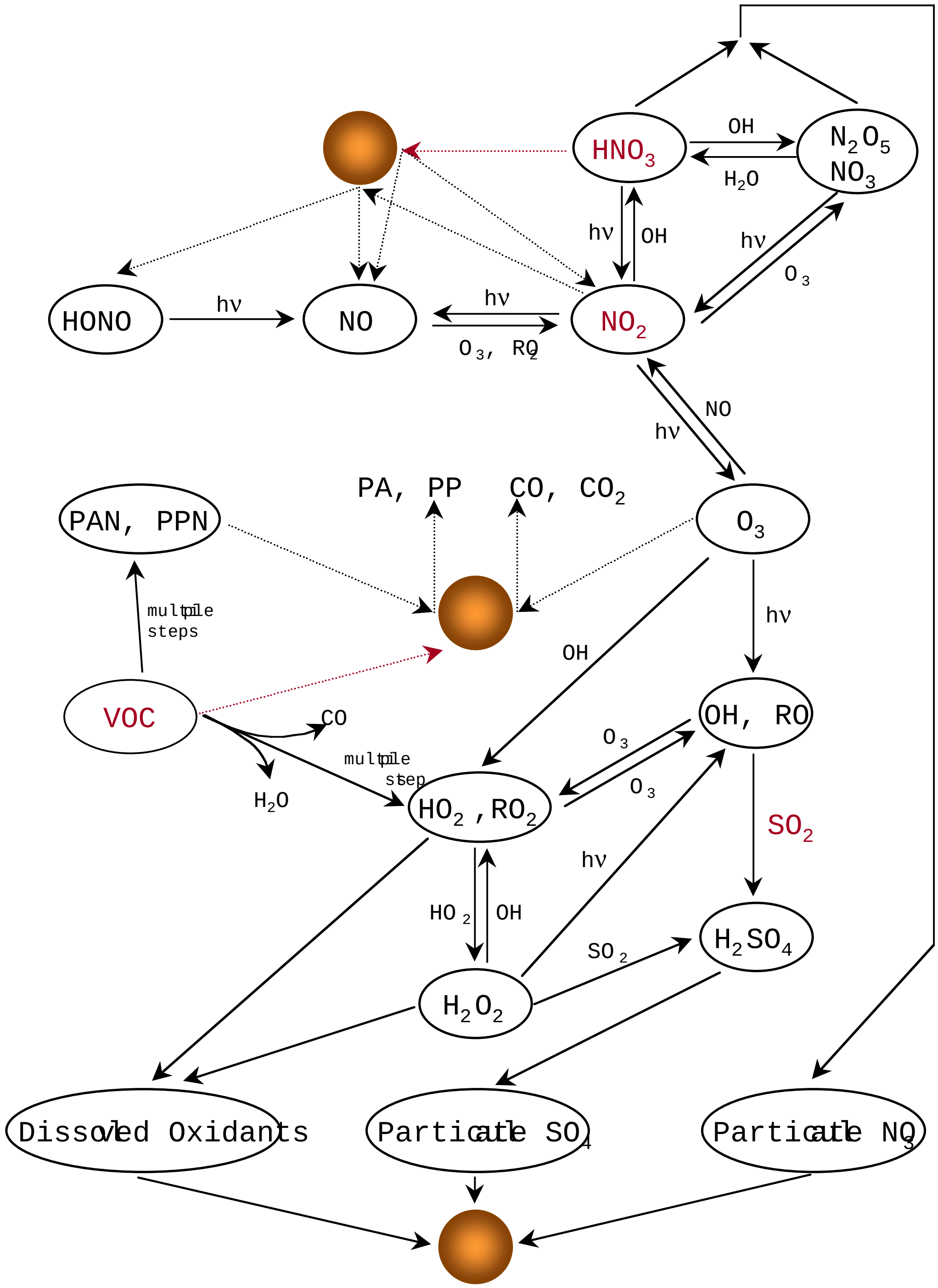
readily react with CO_2 in the atmosphere to give surface carbonate

Evidence for this is seen by the production of gaseous CO_2 during HNO_3 uptake
(e.g. $MgCO_3 + 2HNO_3 \longrightarrow Mg(NO_3)_2 + CO_2 + H_2O$)

THE APPROACH



Reactions of Trace Atmospheric Gases with Aerosol Particles



Experimental Considerations

- **Spectroscopic measurements** to provide both qualitative (what reactions are possible) and quantitative information
  - Provide mechanistic information on the molecular level
  - Need to have techniques that can detect gas-phase **and** surface-bound species

Transmission FT-IR Spectroscopy
Diffuse Reflectance UV-vis Spectroscopy
Mass Spectrometry

- **Kinetic measurements** to provide quantitative information
  - Determine uptake coefficients (sticking coefficients, reaction probabilities) γ
- **Provide data as input for global atmospheric models** - removal rate of gas-phase species j

$$k_j = \int_{r_1}^{r_2} k_{d,j}\,(r)\; n(r)\; dr$$

n(r)dr = number density of particles between r and r+dr

$$k_{d,j} = \frac{4\pi r^2 D_j V}{1 + K_n\,(\lambda + 4(1-\gamma)/3\gamma)}$$

What are the Challenges in Laboratory Measurements Of Heterogeneous Reactions on Solid Particles?

- What is the best technique suitable for these
- measurements?

- What is the available surface area?

- Are these reactions stoichiometric or catalytic, i.e.
- does the surface become deactivated with time?

- What is the effect of aging on particle reactivity?

- How can we take these effects into account in laboratory studies?

Methods Used to Measure Heterogeneous Reaction Kinetics on Mineral Dusts

- Knudsen Cell (powders) - dry conditions

- Time-course FT-IR measurements (powders) - dry and wet conditions

- Aerosol Chamber (suspended particles) - dry and wet condtions
- Single Particle Analysis Using SEM and AFM

Laboratory Studies Designed to Provide Useful Information for Atmospheric Chemistry Models

1. **Heterogeneous Uptake of Organic and Inorganic Acids**

2. **SO_2 Uptake on Mineral Dust**

3. **Heterogeneous Reaction of Ozone on Mineral Dust**

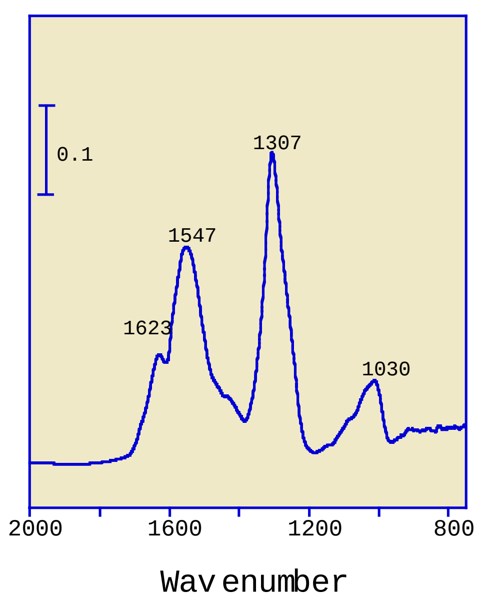
Heterogeneous Reactions of Inorganic and Organic Acids

HNO_3 and CH_3COOH

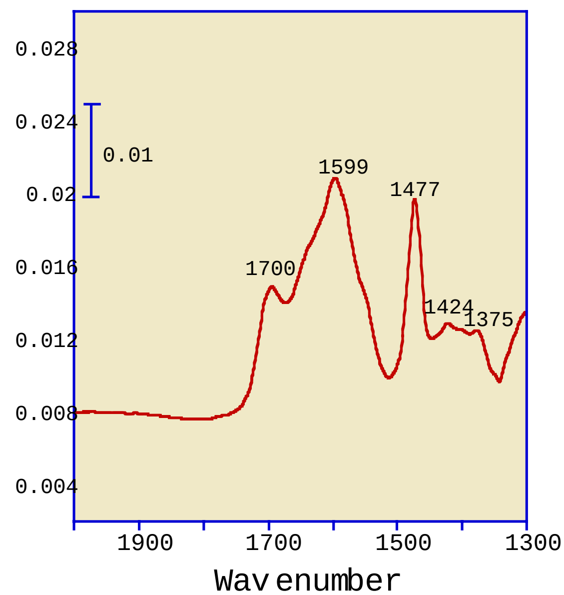
Mostly find irreversible, <u>dissociative</u> adsorption (with the exception of SiO_2) leads to the formation of adsorbed nitrate and acetate, respectively, as determined by FT-IR spectroscopy

α-Al_2O_3

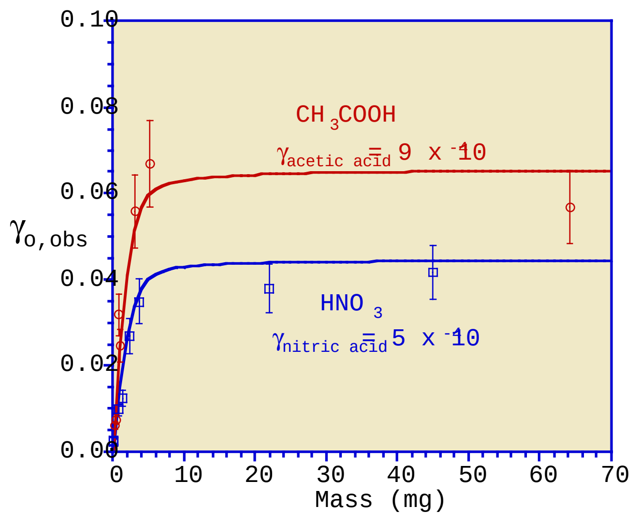
Adsorbed Nitrate



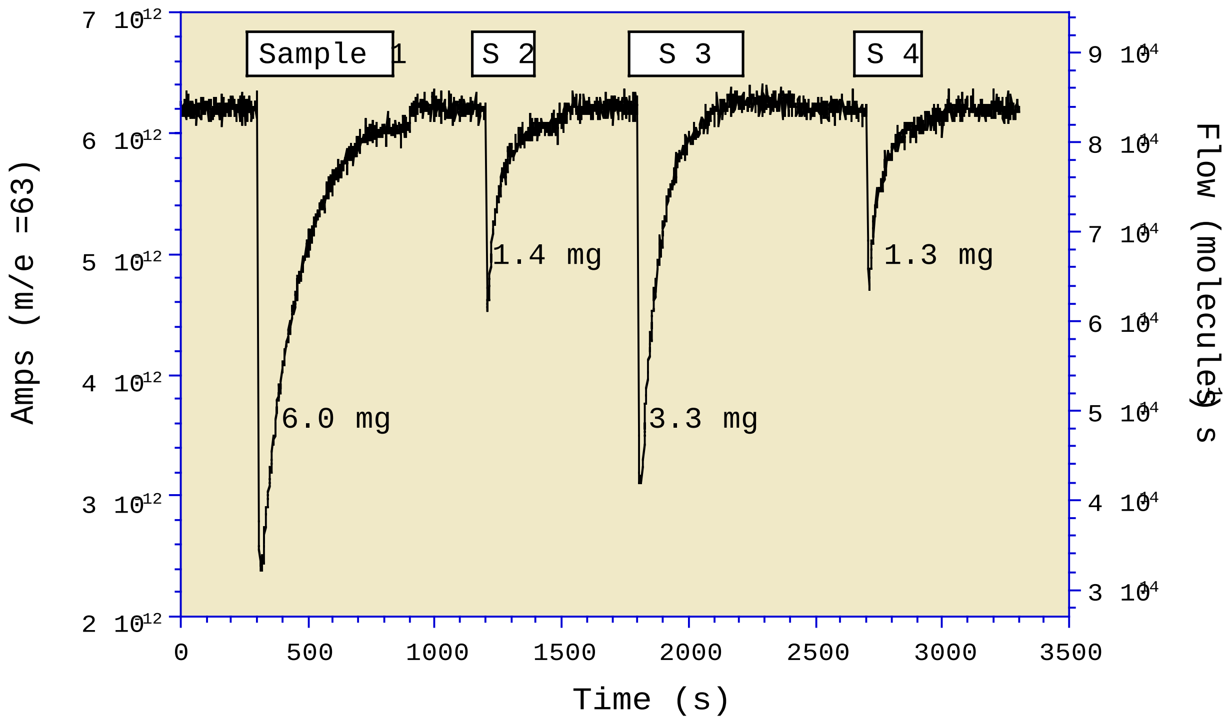
Adsorbed Acetate

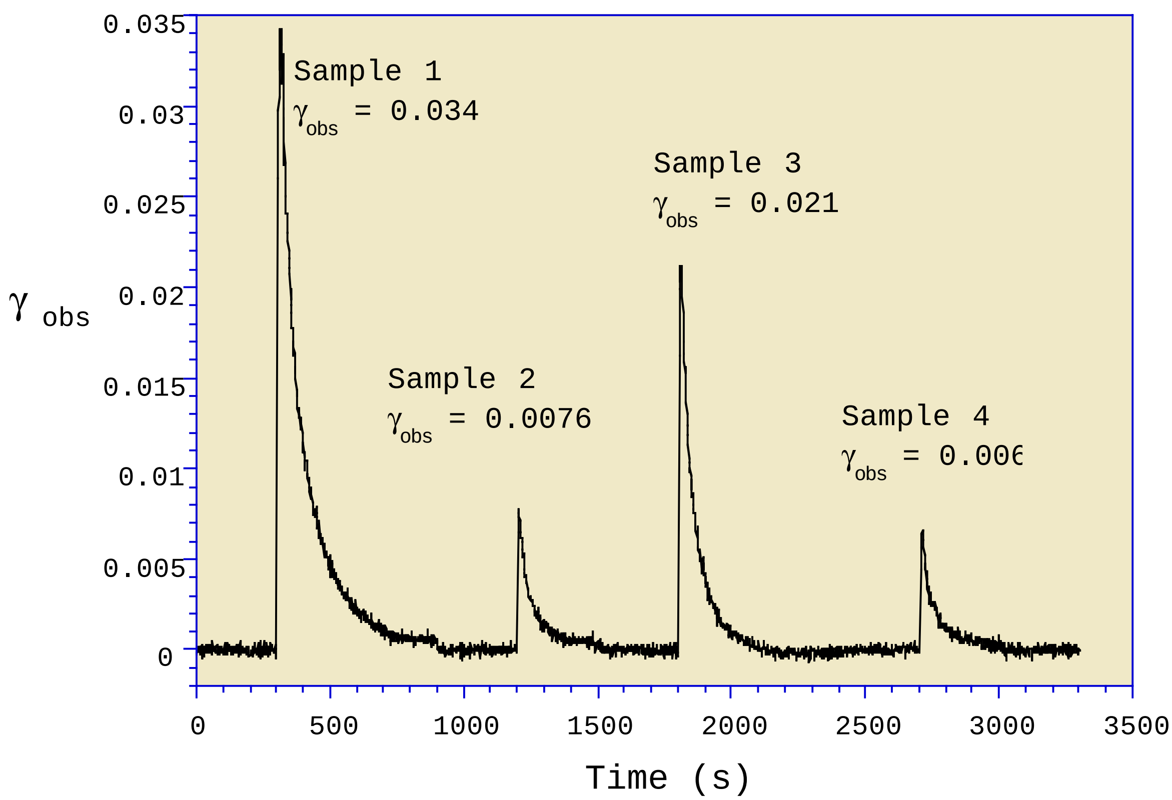


Kinetic Data

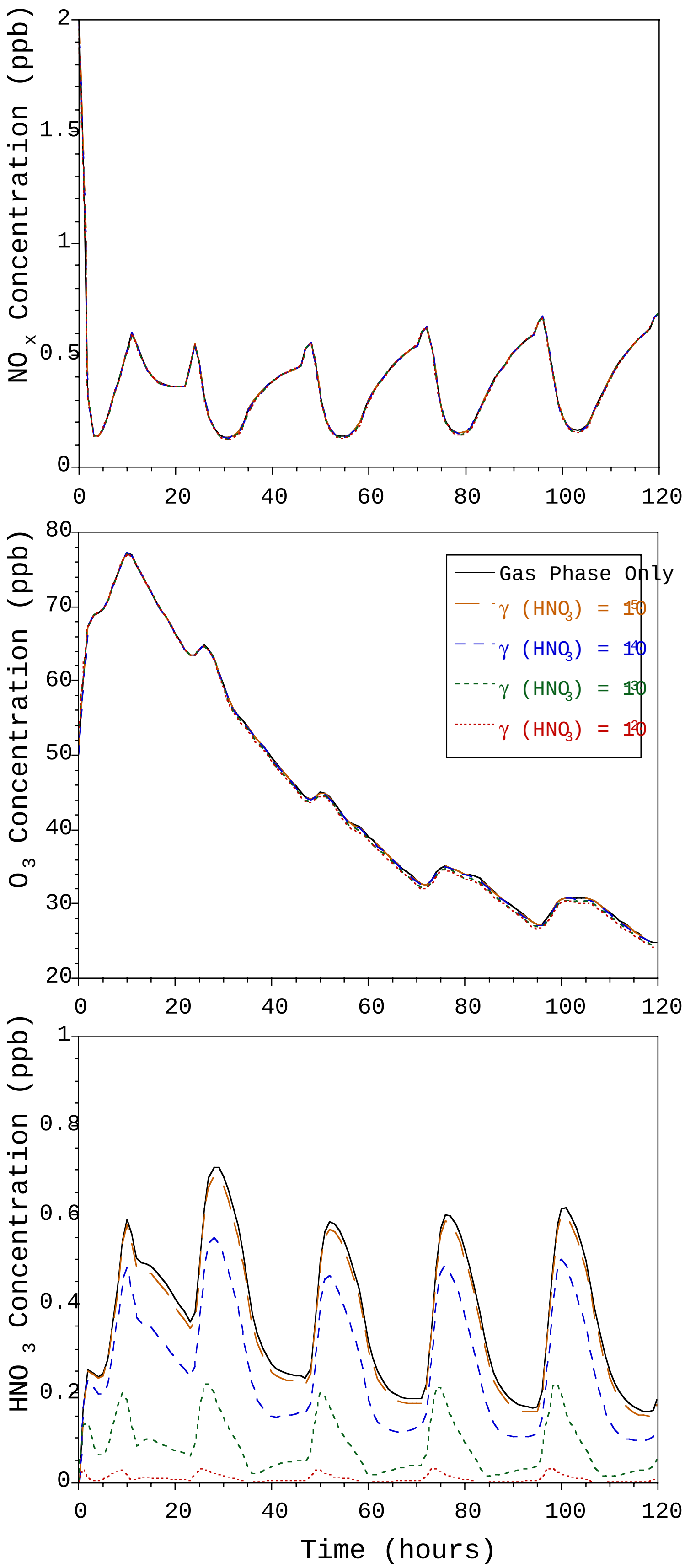


Nitric Acid Uptake on α-Al_2O_3

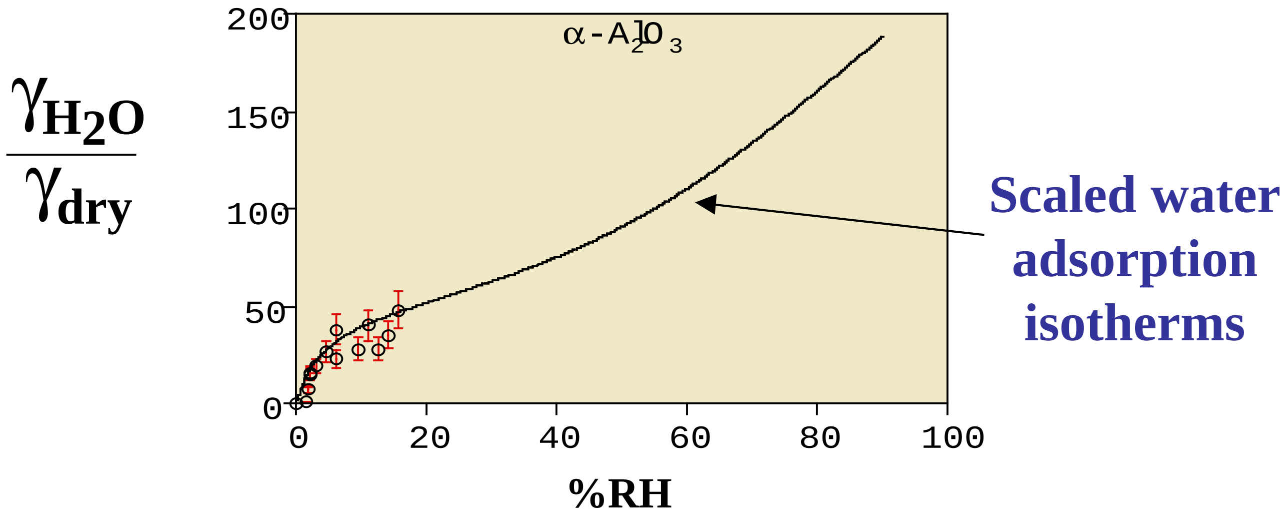




Heterogeneous Uptake of HNO_3 with Surface Saturation

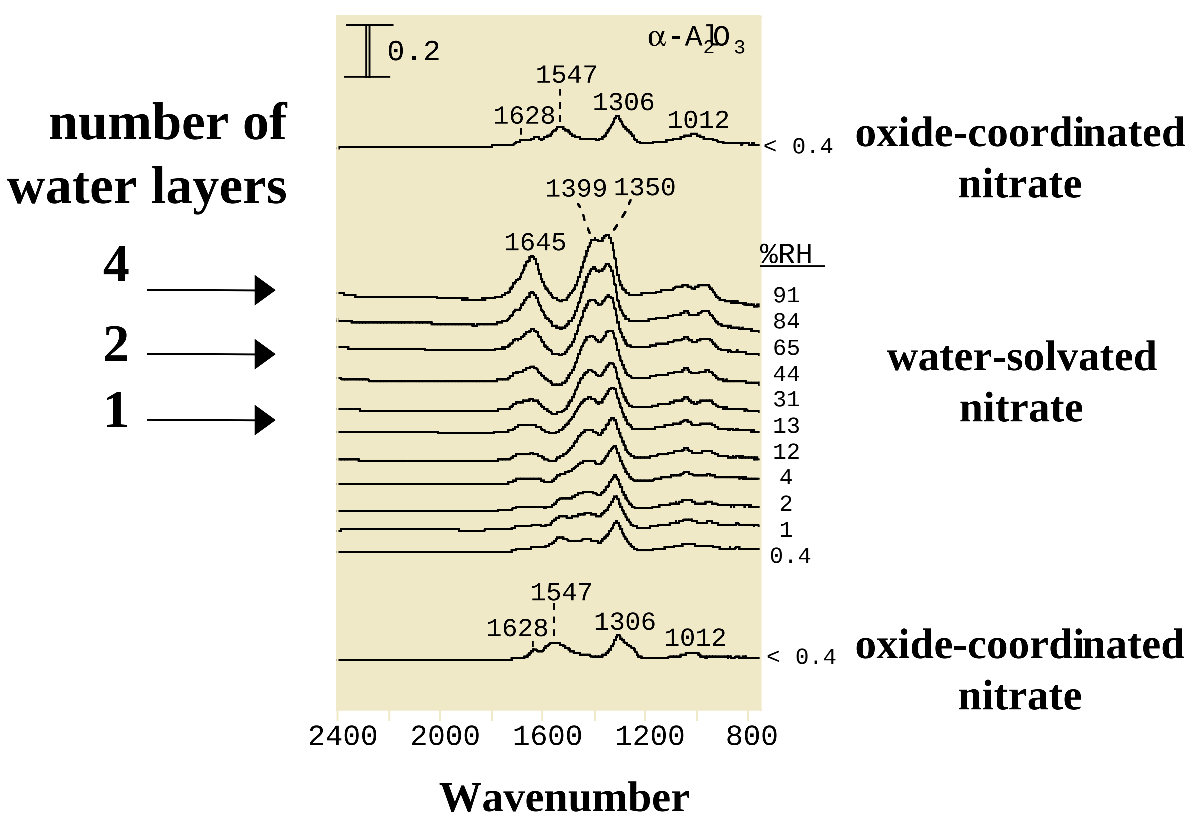


Enhanced Nitric Acid Uptake Kinetics on Oxide Particles in the Presence of Adsorbed Water Measured by FT-IR Spectroscopy



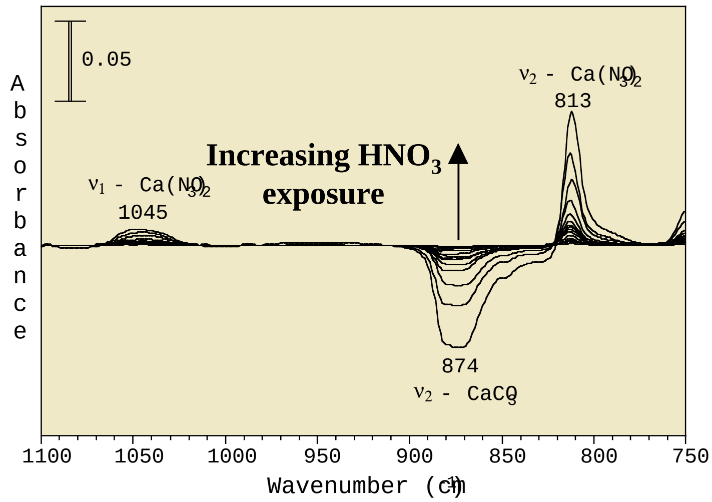
Water adsorption on α-Al_2O_3 following reaction of HNO_3

$$[NO_3^-(a) \rightarrow NO_3^-(a,aq)]$$

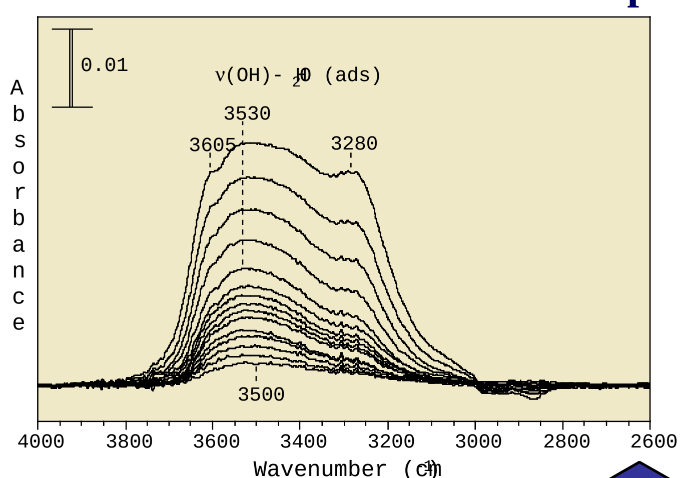


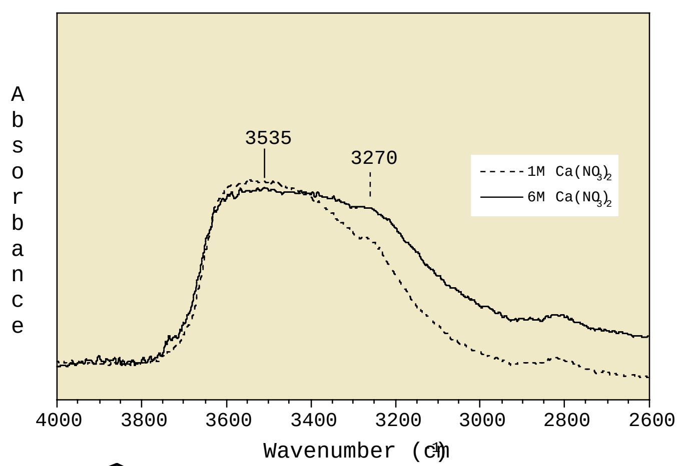
Importance of Water in the Reactivity of of HNO_3 on $CaCO_3$ at 20% RH

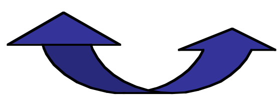
- **No Surface Saturation and Increased Reactivity in the Presence of Water**



2. There is Enhanced Water Adsorption as Nitric Acid Reacts with $CaCO_3$



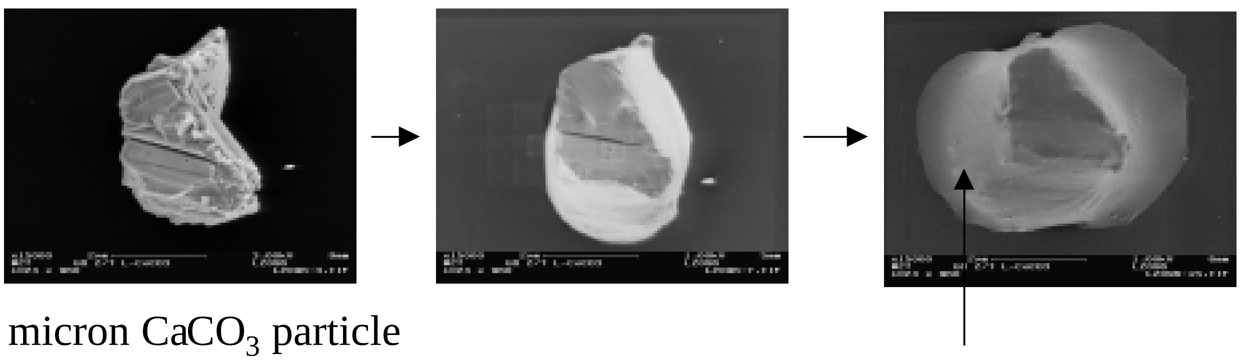




"Adsorbed Solution" and Liquid Solution Spectra Are Similar

Single Particle Analysis Studies of Heterogeneous $HNO_3/CaCO_3$ Reactions

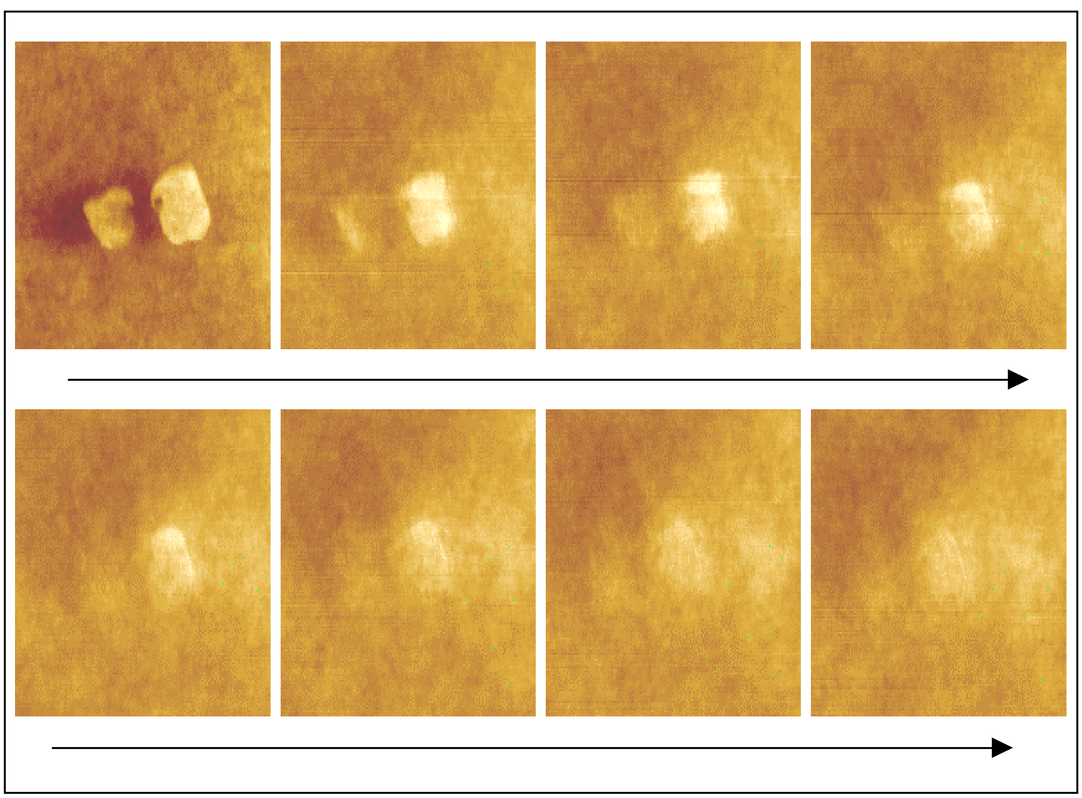
Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis



2 micron $CaCO_3$ particle

$Ca(NO_3)_2$

Atomic Force Microscopy



Measured Initial Heterogeneous Uptake Coefficients (γ_{BET}) for SO_2 on Mineral Dusts

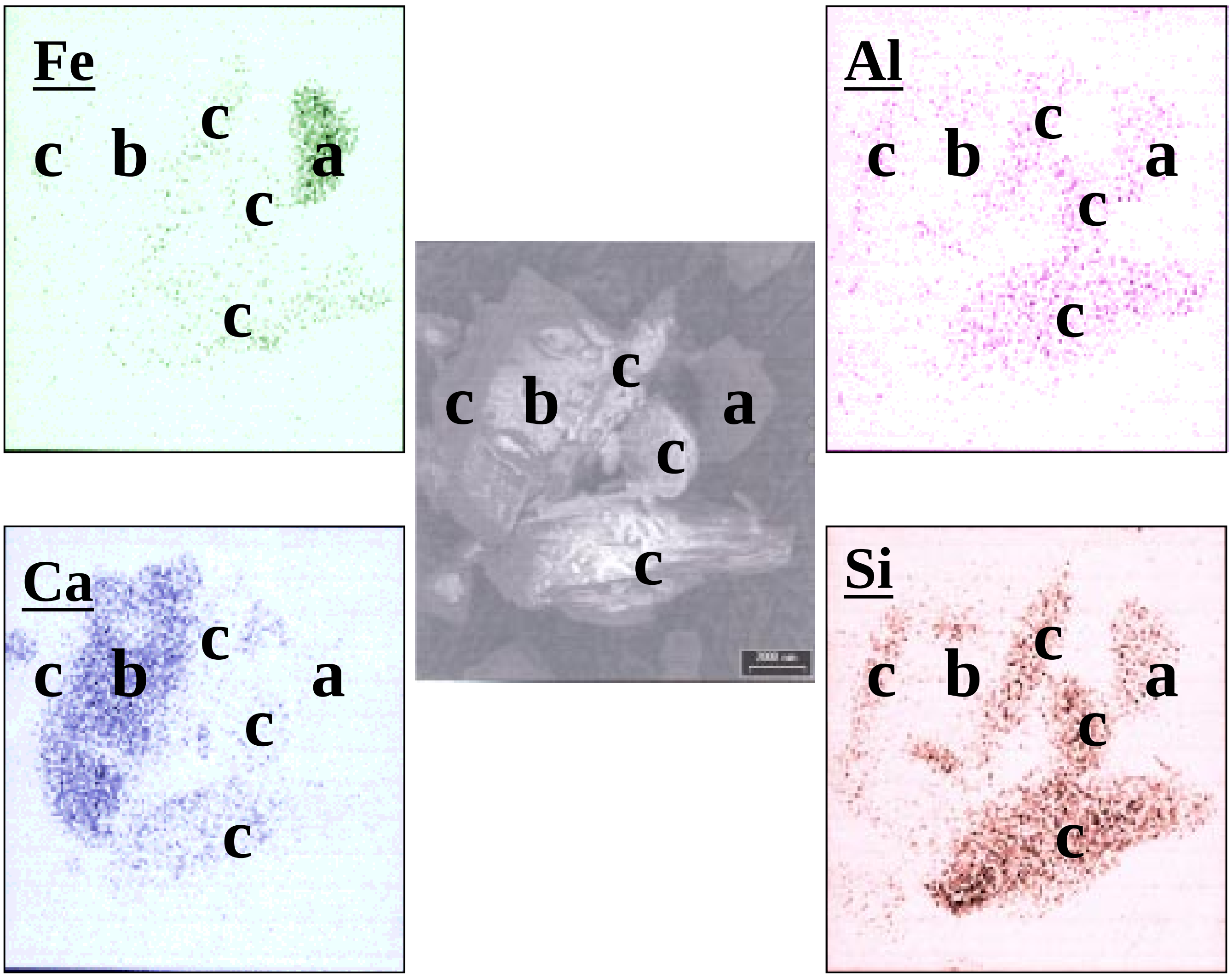
Sample	Uptake Coefficient
TiO_2	$1.0 \pm 0.2 \times 10^{-4}$
$CaCO_3$	$1.3 \pm 0.7 \times 10^{-4}$
α-Fe_2O_3	$7 \pm 2 \times 10^{-5}$
MgO	$5 \pm 1 \times 10^{-4}$
α -Al_2O_3	$2 \pm 1 \times 10^{-4}$
SiO_2	$< 1 \times 10^{-7}$
China Loess	$3 \pm 1 \times 10^{-5}$

Authentic Sample -

China Loess - consists of 48% Si, 22% Ca, 10% 0Fe, 10% Al, 2%Mg and 1% Ti

SEM images and Elemental Mapping (EDXA) show that only certain particles or certain regions of particles will be reactive

SEM Image and 2-D EDX Maps of Dust Particles



Predicted vs. Measured Reactivity

- **Assume Loess sample is composed of an external mixture of single component oxides and carbonates**

$$\gamma_{loess} = \sum_i f_i \gamma_i$$

where f_i and γ_i are the fractional amount and uptake coefficient, respectively, of component *i*.

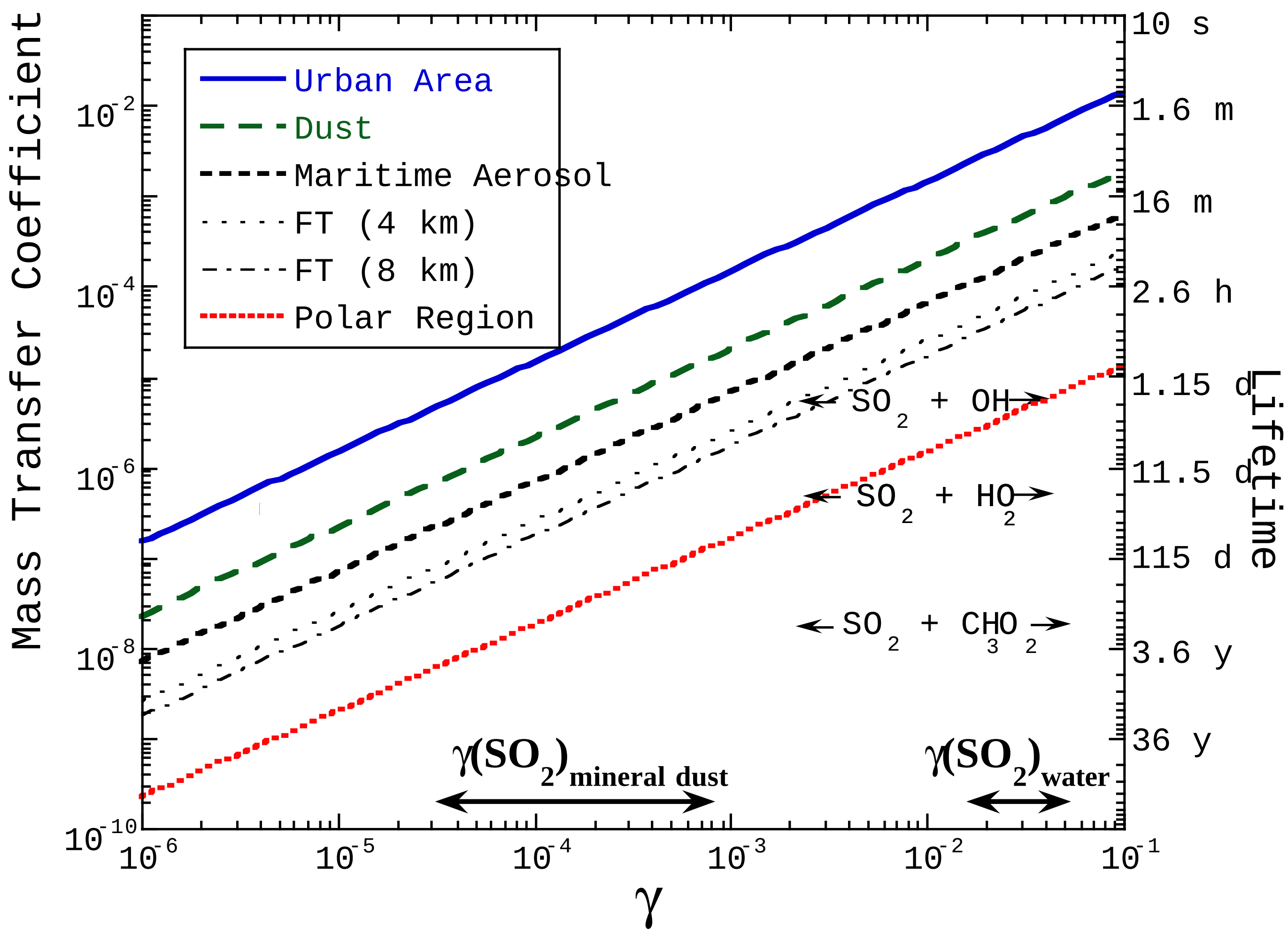
$$\gamma_{\mathbf{predicted}} = \mathbf{4 \pm 2 \times 10^{-5}}$$

- **Measured Reactivity**

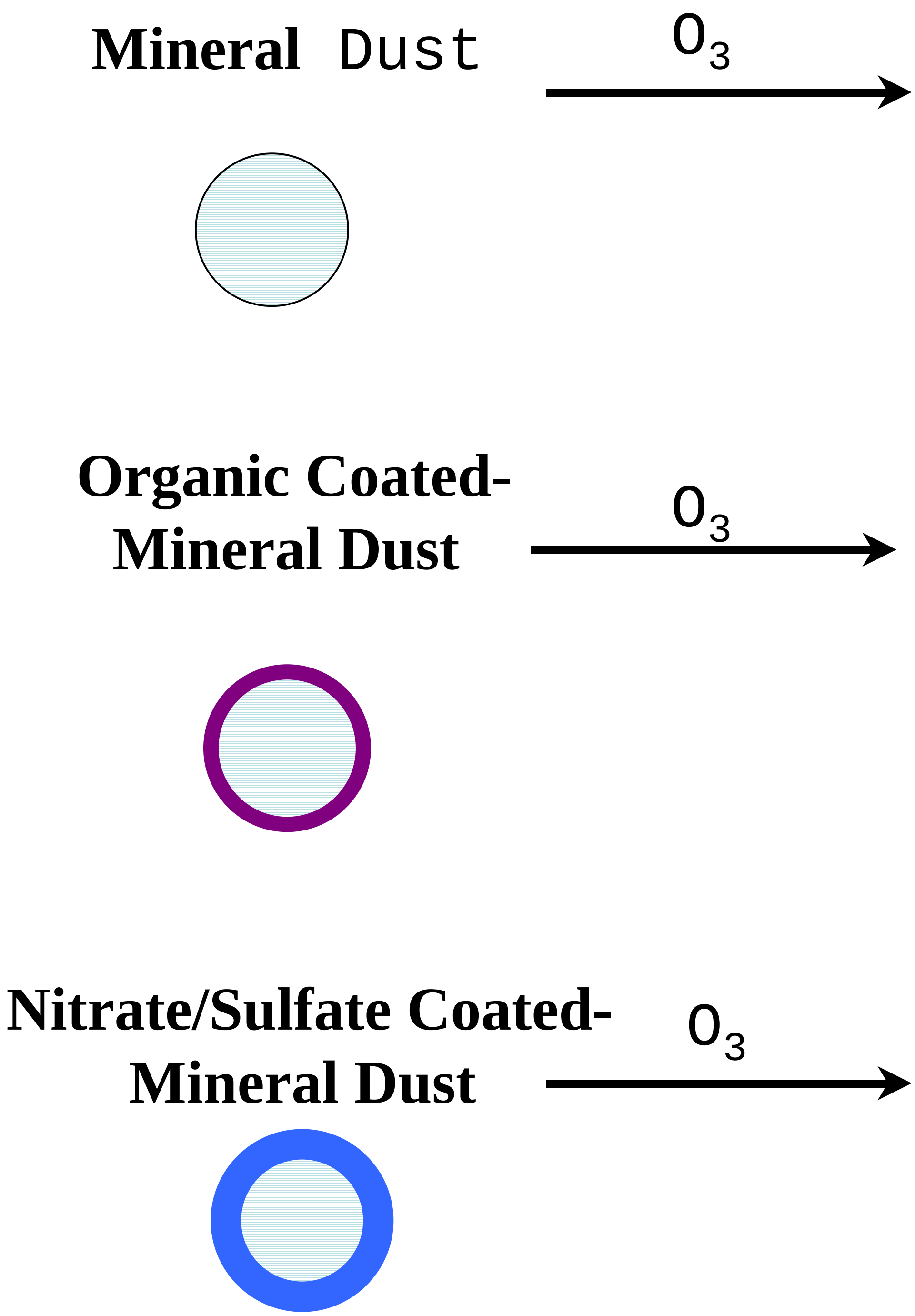
$$\gamma_{\mathbf{measured}} = \mathbf{3 \pm 1 \times 10^{-5}}$$

- **This suggests that the surface area of each component is similar and the surface and bulk compositions are similar**

Comparison to Other Loss Mechanisms



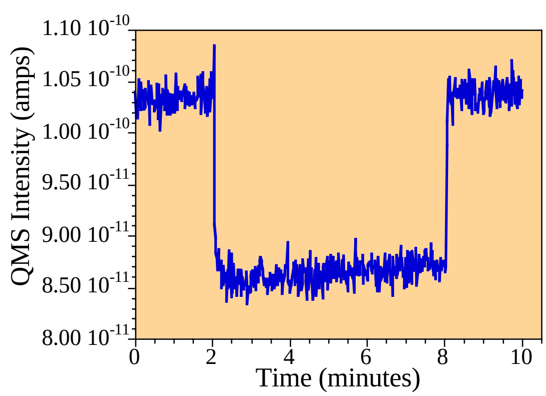
Reactivity of Mineral Dust Aerosol With Ozone



Ozone Uptake and Destruction on Mineral Dust

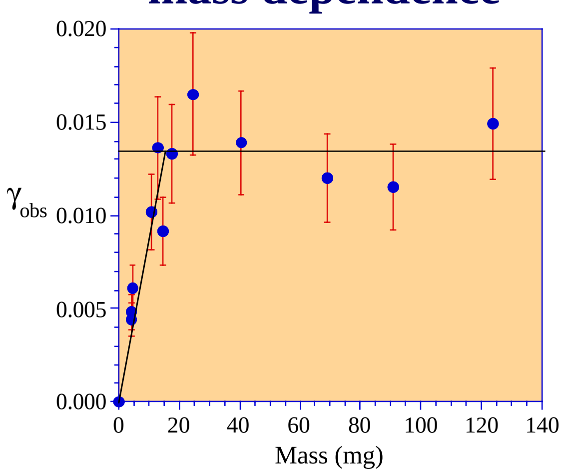
- **Ozone uptake on α-Al_2O_3, α-Fe_2O_3, SiO_2**
- **Ozone uptake on Sarahan Sand**

α-Fe_2O_3

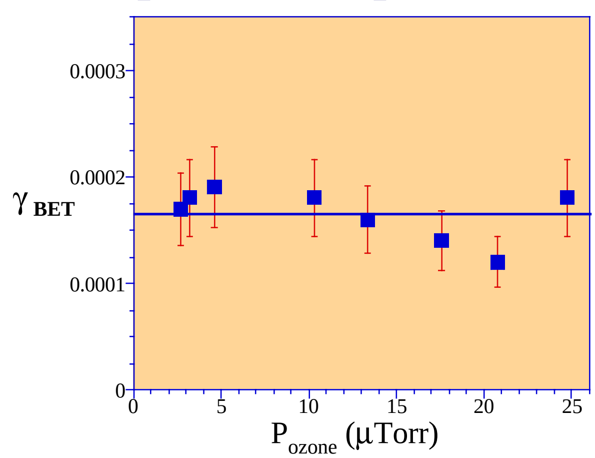


Initial γ

mass dependence



pressure dependence



$$\gamma_{BET} = 1.6 \times 10^{-4}$$

Summary of Ozone Uptake on Mineral Dust

Kinetic Data

Sample	$\gamma_{0,\,BET}$
α-Al_2O_3	$8 \pm 5 \times 10^{-5}$
α-Fe_2O_3	$1.8 \pm 0.7 \times 10^{-4}$
SiO_2	$5 \pm 3 \times 10^{-5}$
Saharan sand	$6 \pm 3 \times 10^{-5}$

Total Uptake of O_3 Exceeds 10^{15} molecules cm^{-2}

Ozone Destruction is Catalytic

Summary

- Organic and inorganic acids have high reactivity and are both taken up by dust particles. The uptake of nitric acid increases as the relative humidity increases showing the importance of water adsorbed on the particles in these reactions.
- On $CaCO_3$ and some oxides, the reactivity of HNO_3 is not limited to the surface of the particle but occurs into the bulk
- SO_2 uptake on solid particles is lower than on liquid droplets
- Authentic dust samples are composed of particles and regions of particles with different reactivity. The laboratory studies show that to a first approximation the reactivity of authentic dust samples can be thought of as an external mixture of oxides and carbonate aggregates of different reactivity. The relative importance of each component is weighted by its natural abundance in the sample.
- Adsorbed S(IV) is oxidized to S(VI) with ozone but not molecular oxygen.
- Ozone uptake is shown to be catalytic on mineral dust particles under the conditions of this study.

HNO_3 Adsorption on Oxide and Carbonate Particles (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO and MgO)

- Unreactive Insoluble

SiO_2

Reversible

Molecular

Adsorption

$HNO_3(a)$

Surface limited

- Reactive Insoluble

α-Al_2O_3

α-Fe_2O_3

TiO_2

Irreversible

Dissociative

Adsorption

$H^+(a) + NO_3^-(a)$

Surface limited

- Reactive Soluble

$CaCO_3$

CaO

MgO

Dissociative

Adsorption

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

(Ion Exchange-Reaction)

"Adsorbed saturated solutions"

Adsorption not limited to the surface

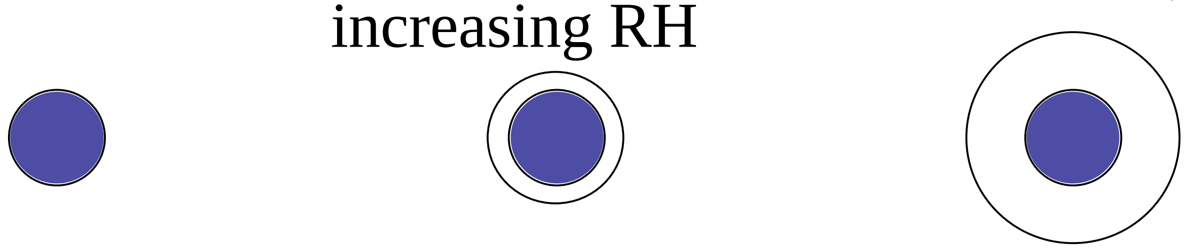
What are mineral dusts composed of and, more importantly what are the surfaces coated with?

- Water
- Organic
- Nitrate
- Sulfate

First consider the role of water in surface reactions (How much water is there?)

tropospheric particle

increasing RH



dry particle

particle with suface adsorbed water

particle immersed in a liquid water droplet

surface sites
defect sites

surface sites, blocked sites
coadsorption

solubility, Ksp
ionic species

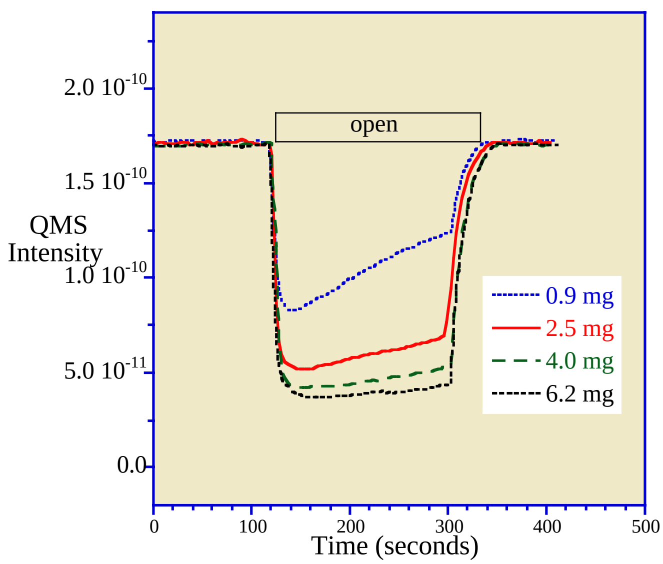
Chemistry of atmospheric gases with the *same* particle may be *different* for each of these conditions

Heterogeneous Chemistry of SO_2 on Oxide and Mineral Dust Particles

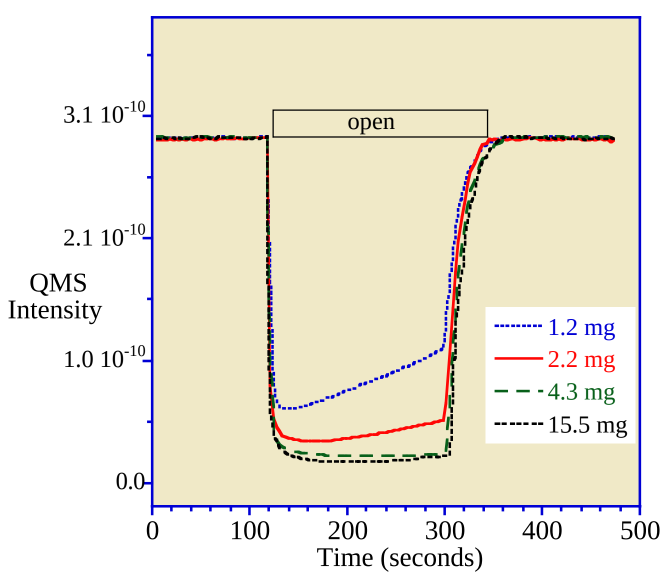
KNUDSEN CELL DATA

•Kinetic data show that the uptake is mass dependent

α-Al_2O_3



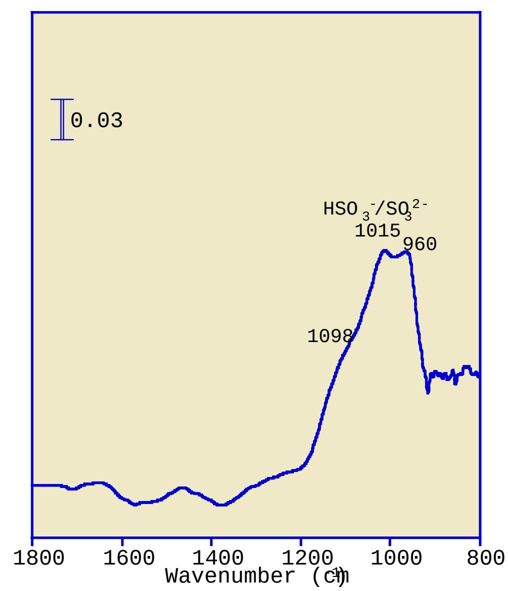
MgO



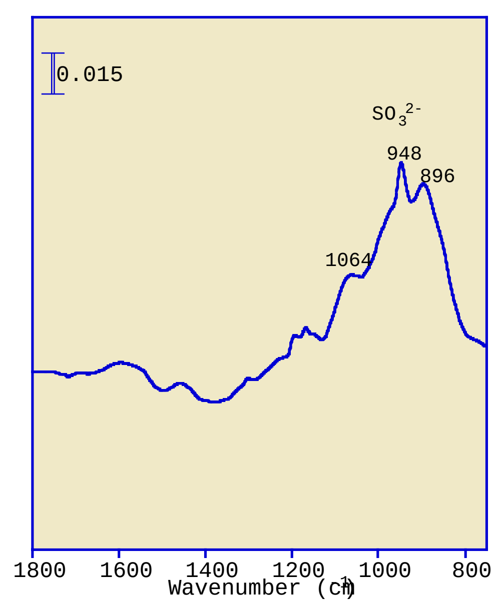
FT-IR DATA

•SO_2 reacts with surface oxygen atoms and hydroxyl groups to form adsorbed SO_3^{2-} and HSO_3^-

α-Al_2O_3



MgO



Surface versus Bulk Compositions

Dust from Sahara and Gobi Deserts

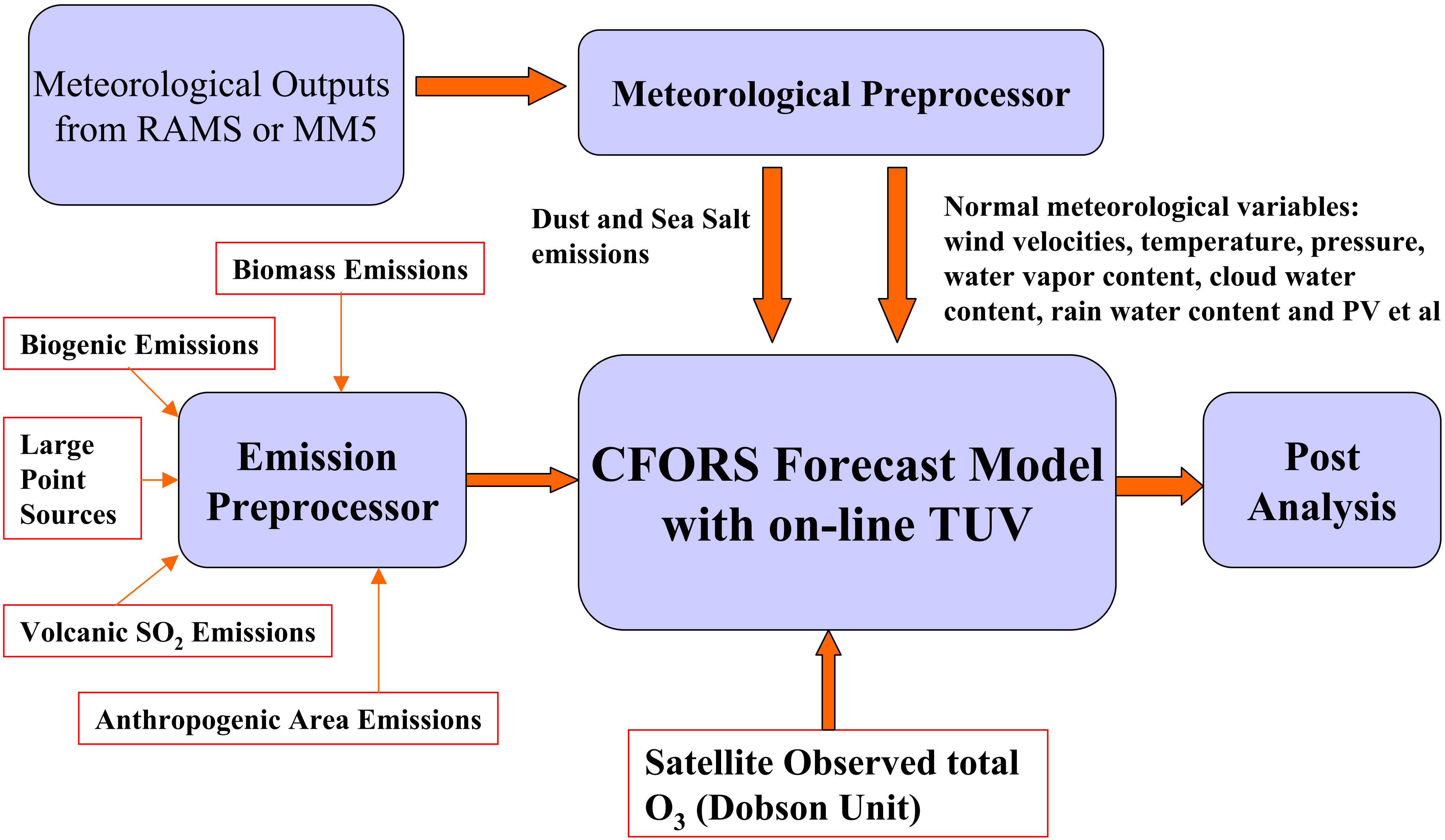
TEM (bulk analysis)
versus
Auger electron spectroscopy (surfaces analysis)

Element	Atom%* (Gobi)		Atom%* (Sahara)	
	Bulk	Surface	Bulk	Surface
Si	48	49	81	76
Al	**10**	**24**	**8**	**15**
Fe	**10**	**3**	**7**	**2**
Ca	**22**	**13**	1	2
Ti	1	0	2	1
Mg	2	7	1	4
K	7	4	2	0

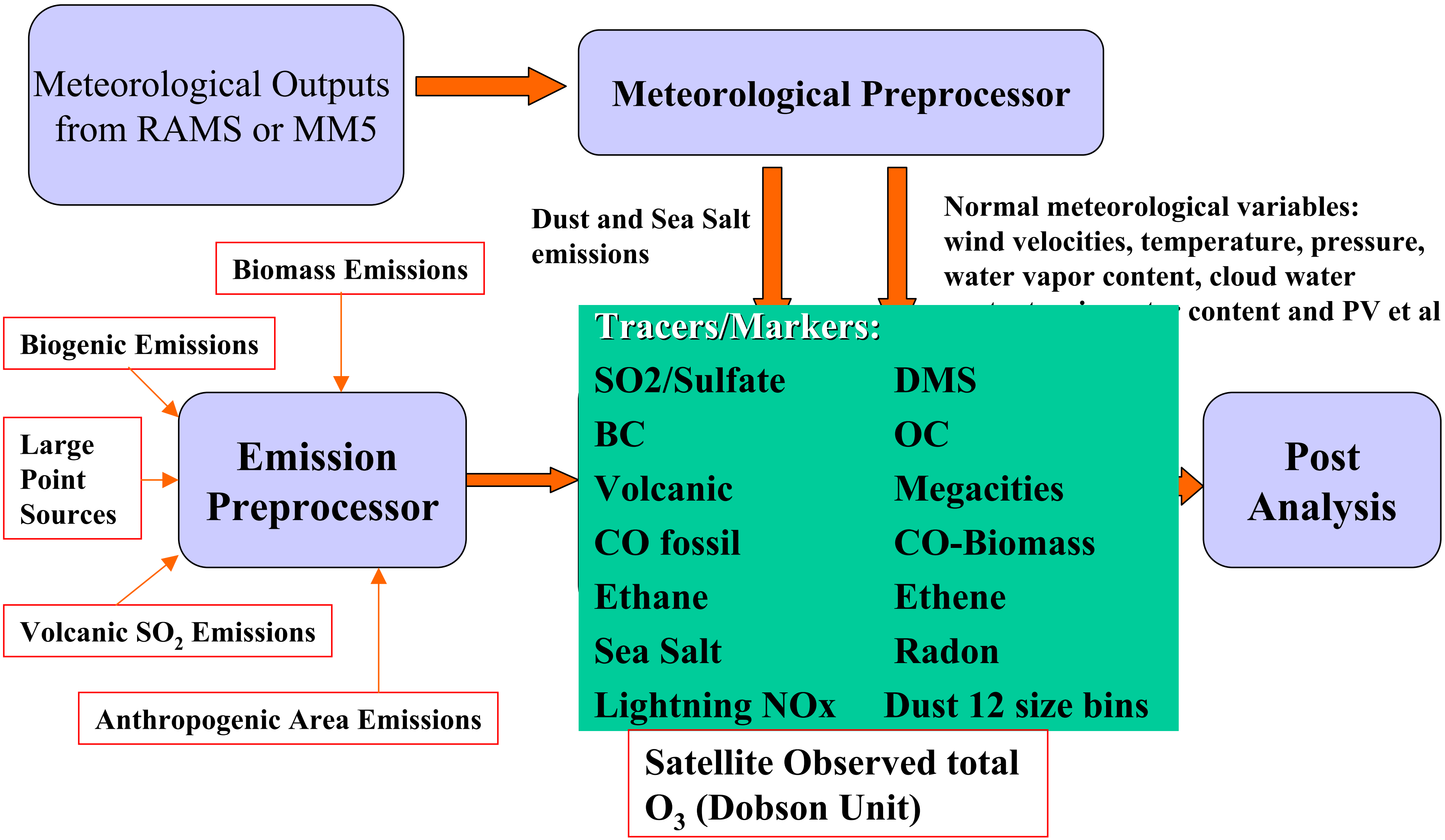
*±2%, systematic errors only

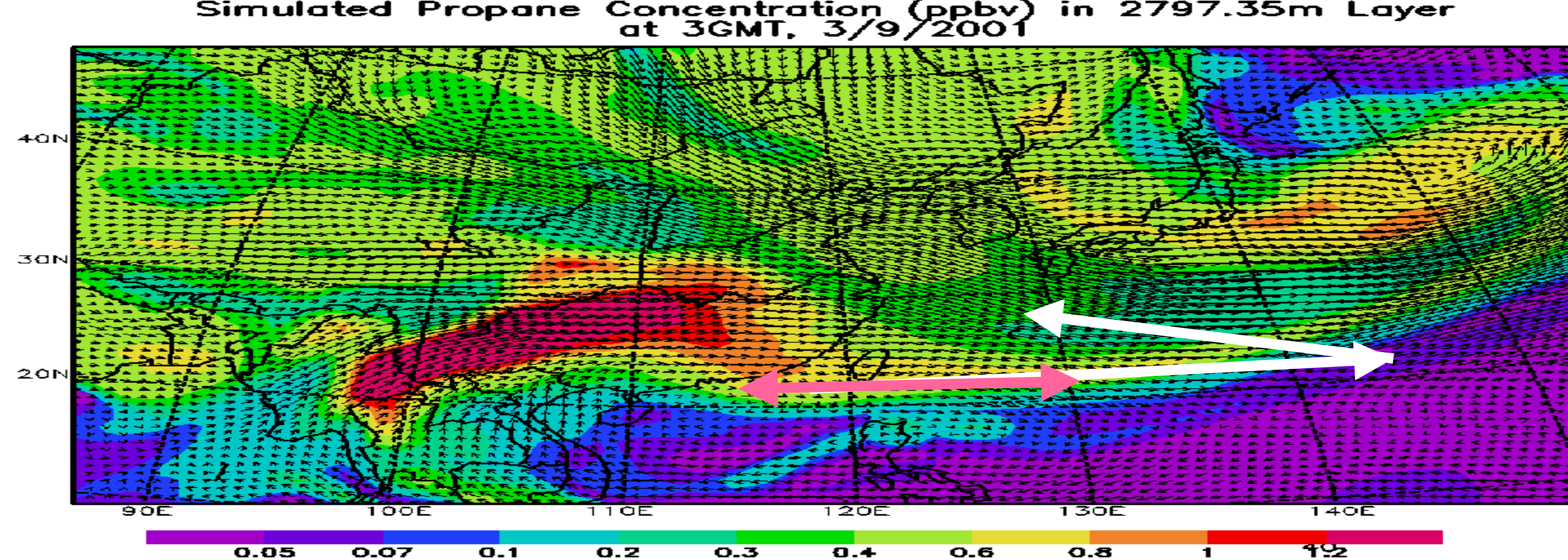
*Data suggest an enrichment in Al at the surface and a depletion in Fe and Ca with the Si content staying approximately the same
*Futher studies are underway

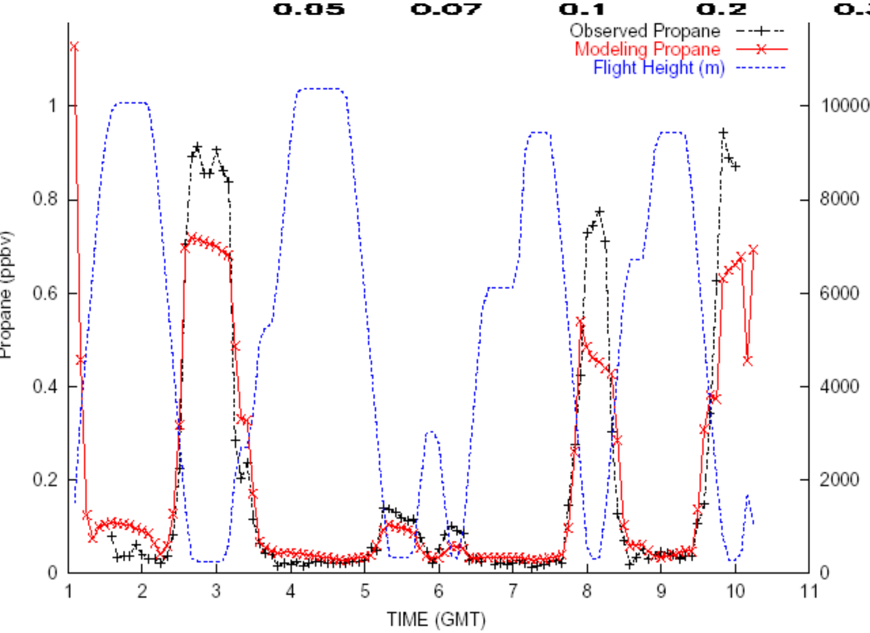
CFORS/STEM Model Data Flow Chart

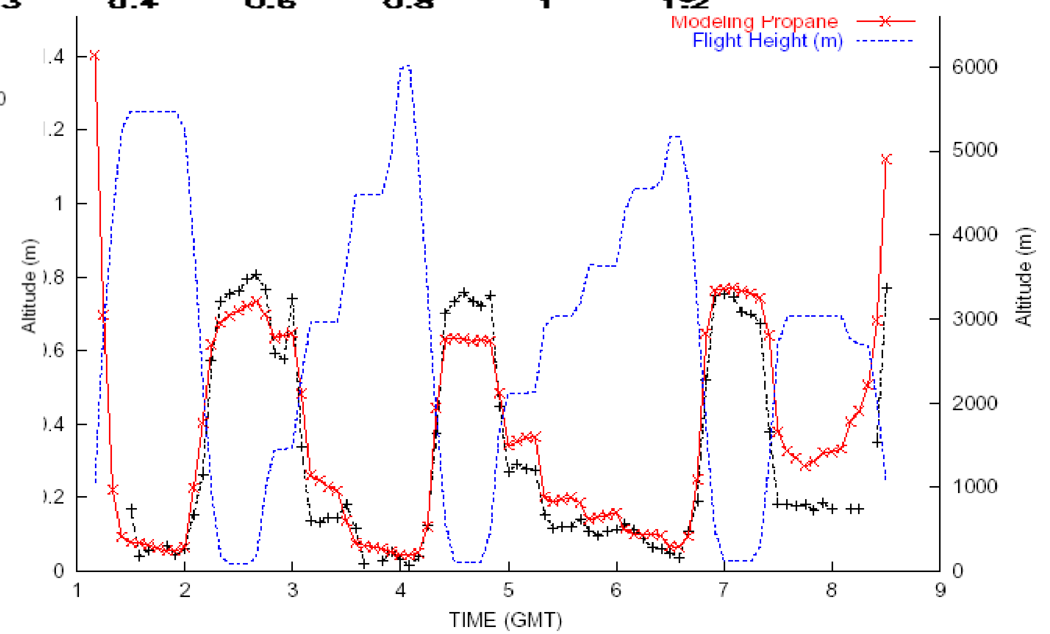


CFORS/STEM Model Data Flow Chart



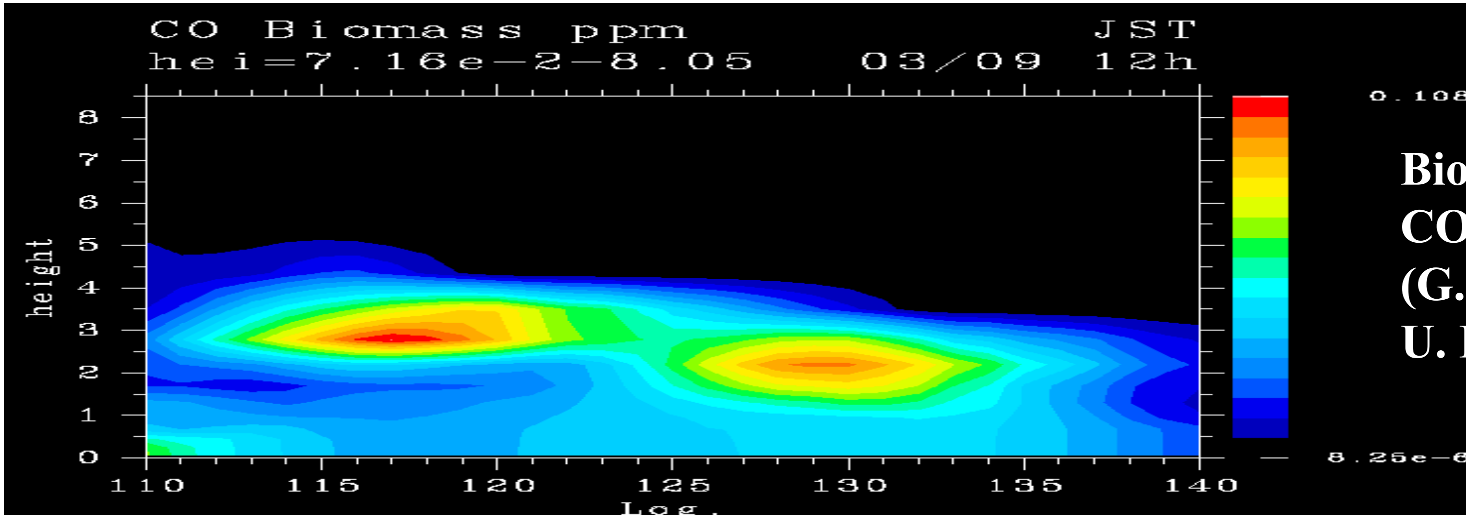




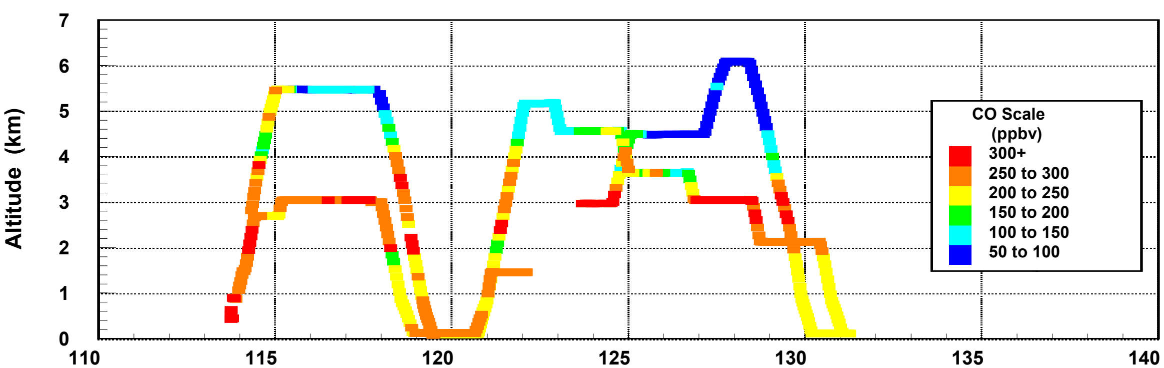


Propane data by Blake et al.

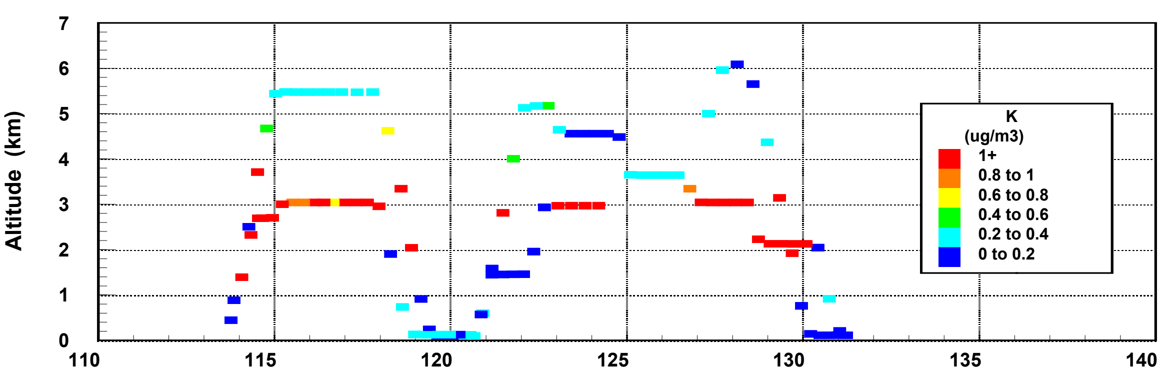
Frontal outflow of biomass burning plumes E of Hong Kong



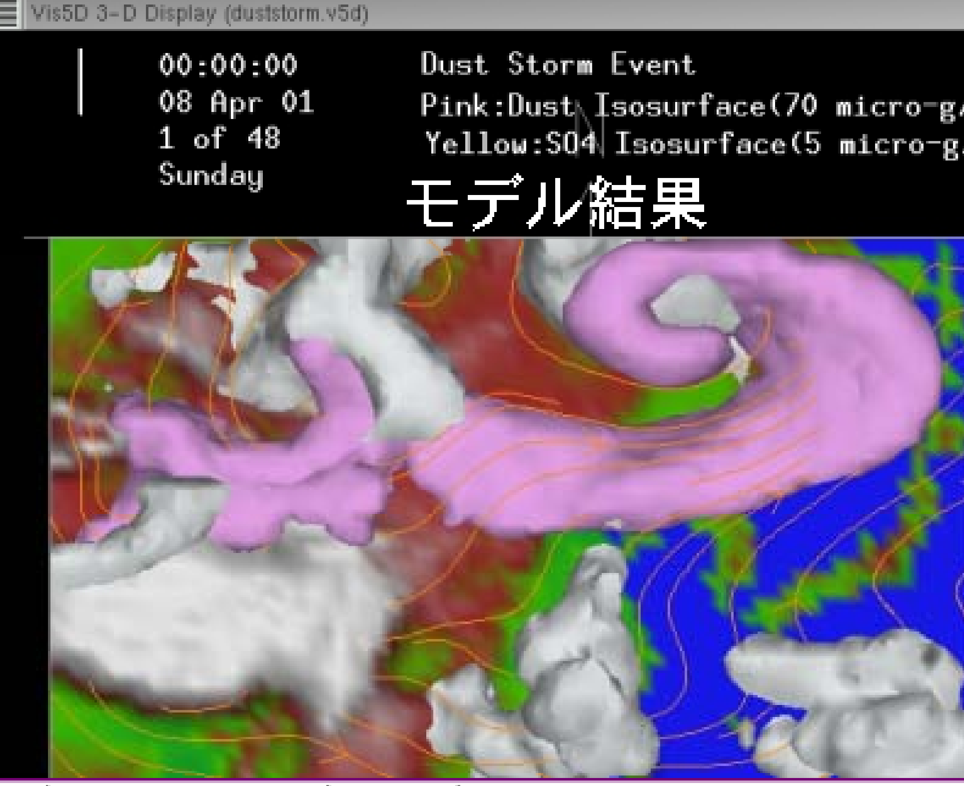
Biomass burning CO forecast (G.R. Carmichael, U. Iowa)

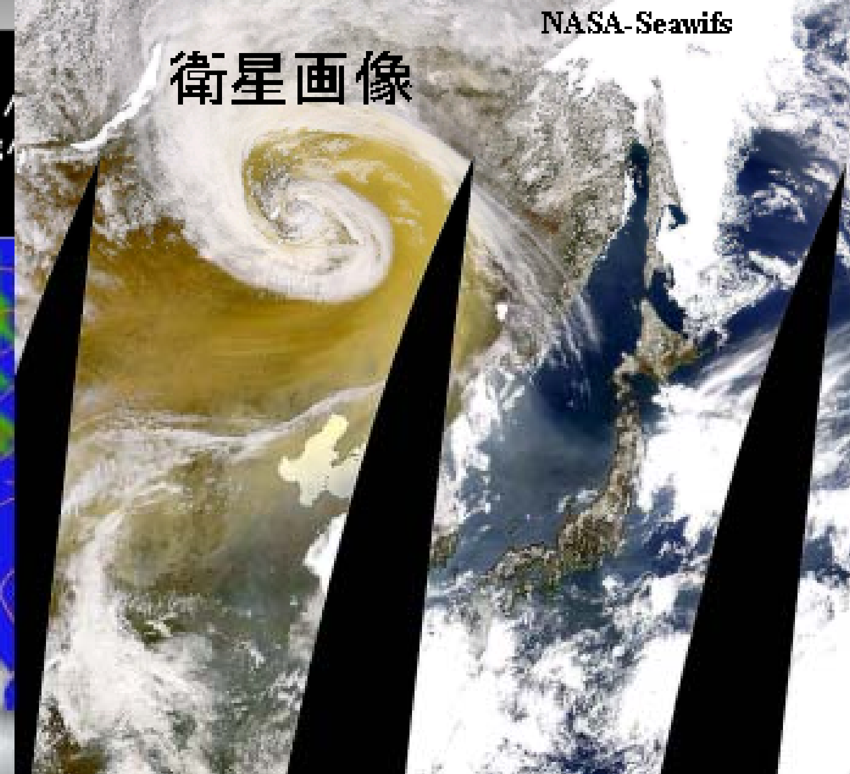


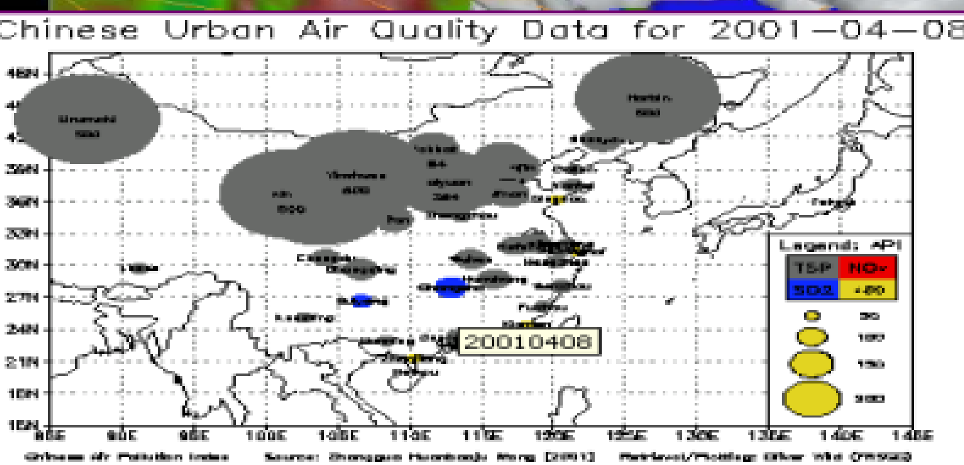
Observed CO (G.W. Sachse, NASA/LaRC)

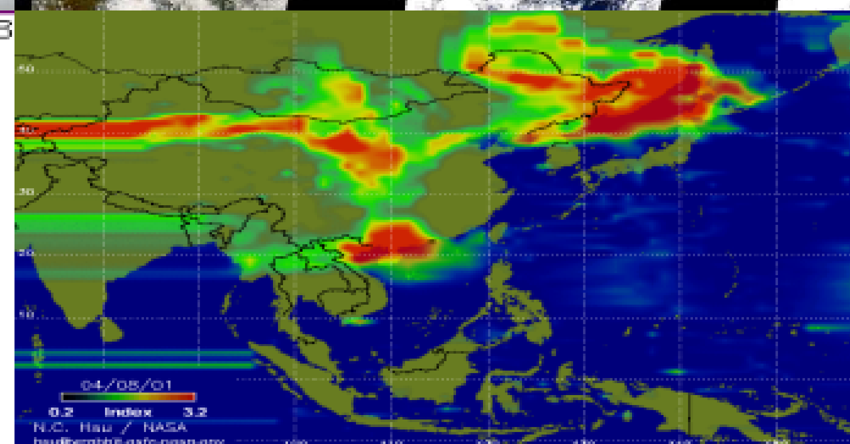


Observed aerosol potassium (R. Weber, Georgia Tech & Y. Lee (BNL))



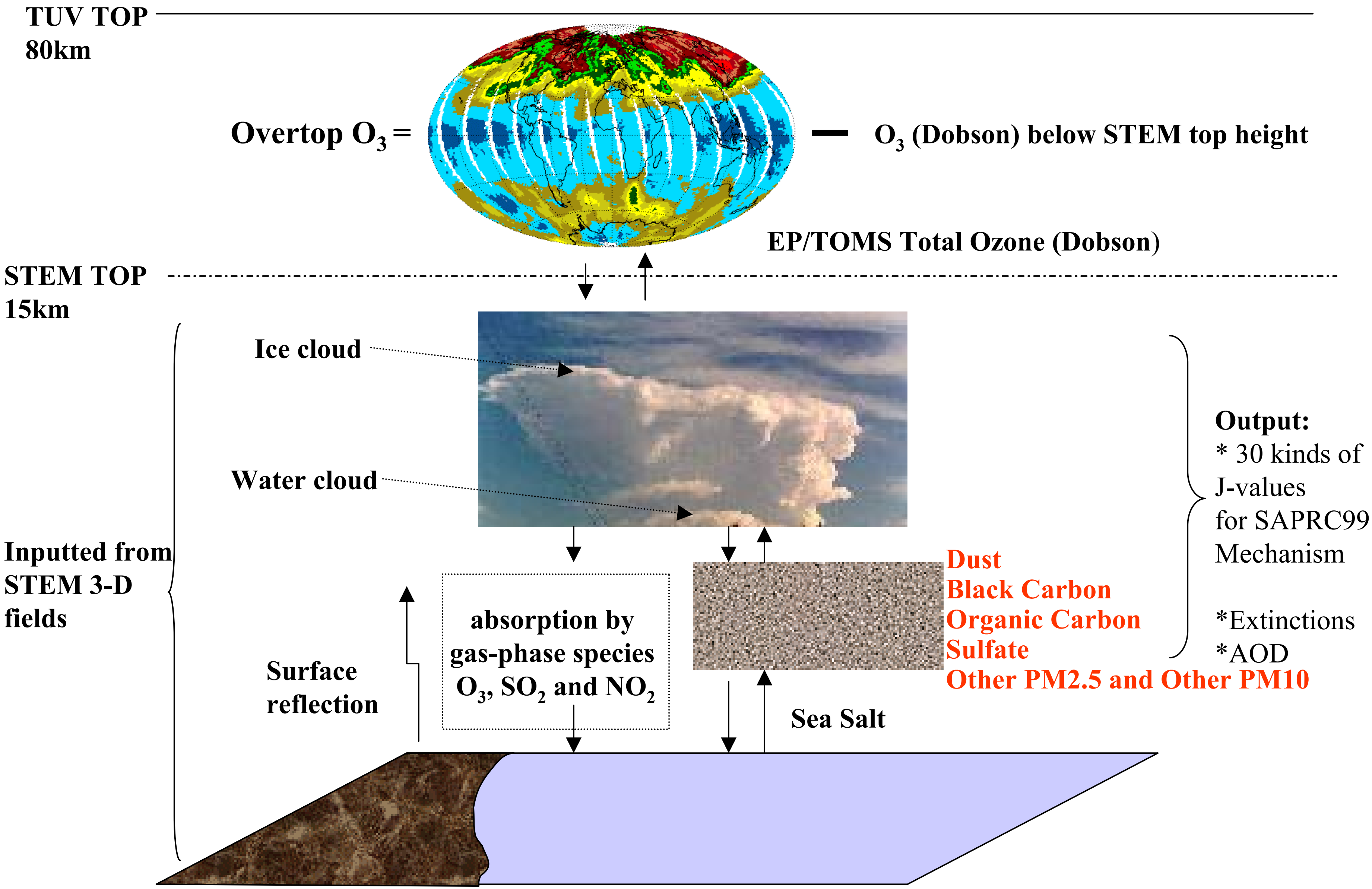




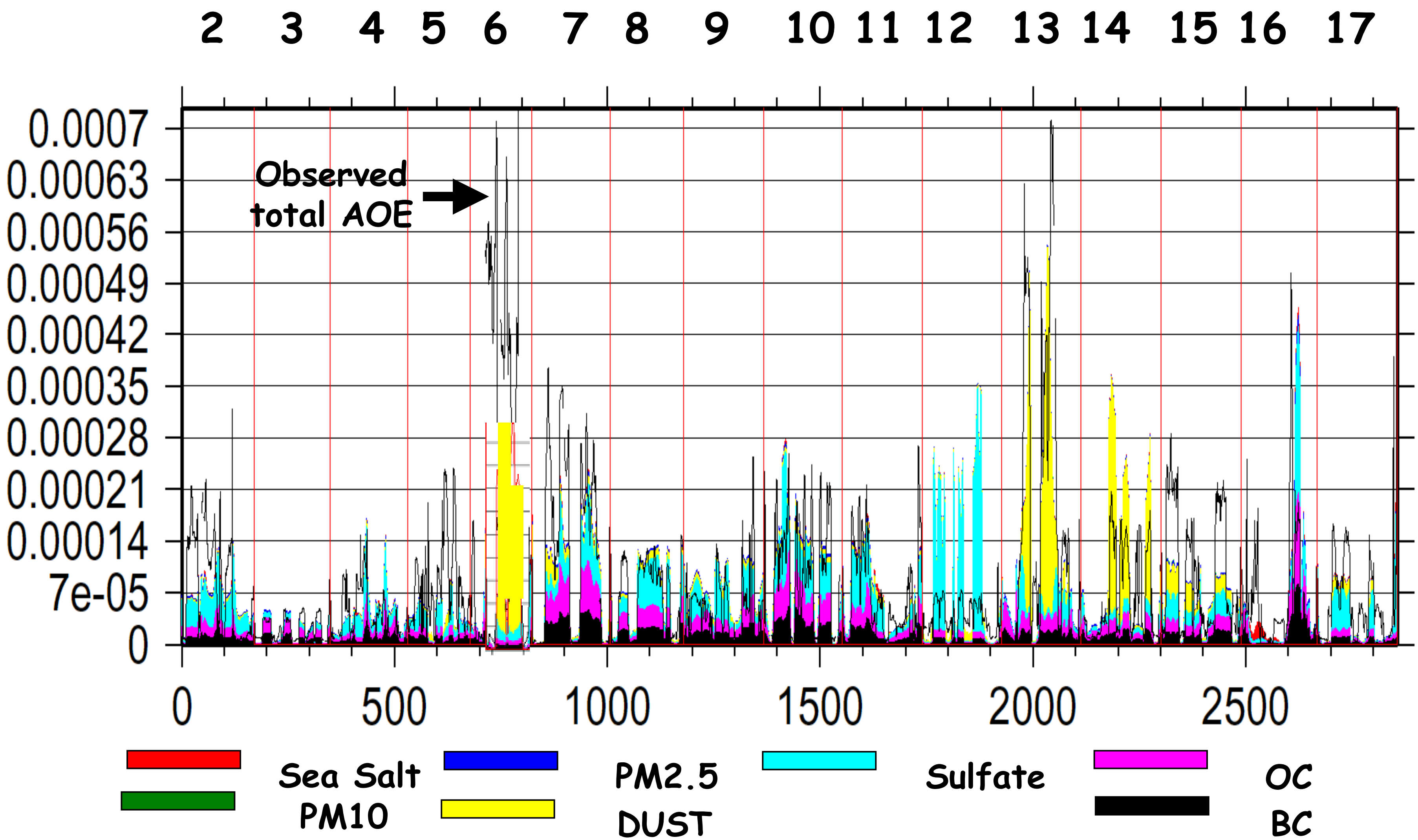


日本列島よりも大きなPerfect Dust Storm

STEM + on-line TUV



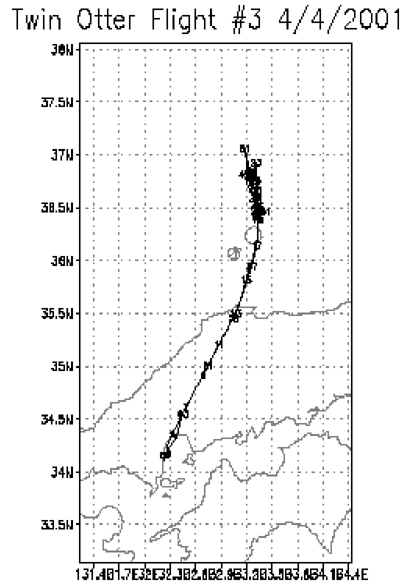
C130 Extinction
(observations from T Clarke and T. Anderson)

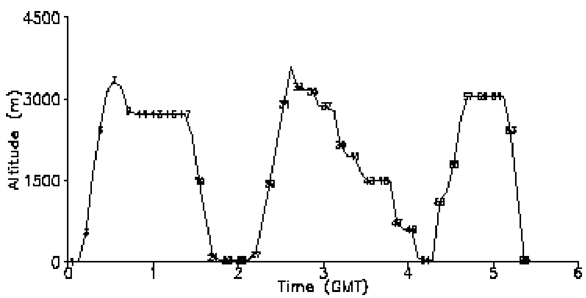


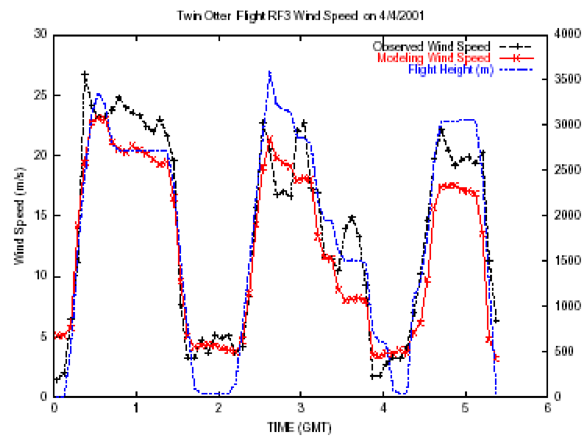
ACE-ASIA Twin Otter Flight RF3

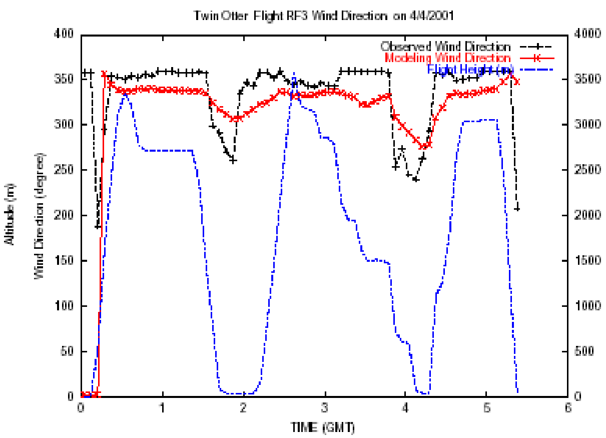
Meteorological Fields for Twin Otter Flights

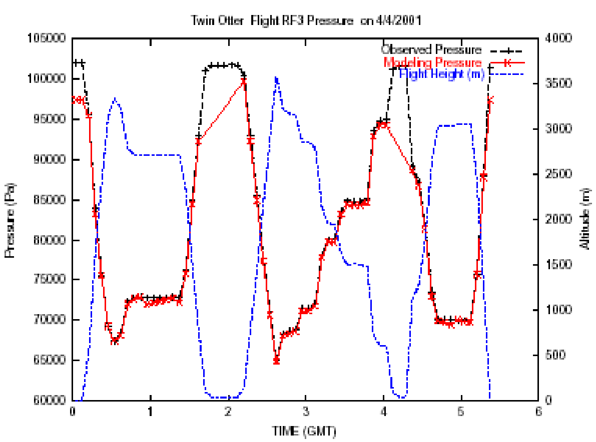
(Seinfeld & Flagan)

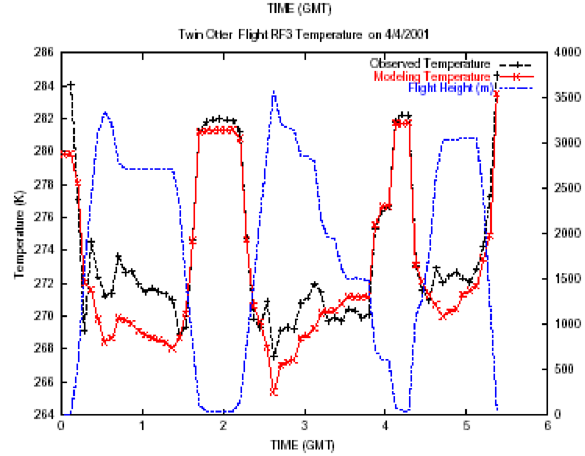


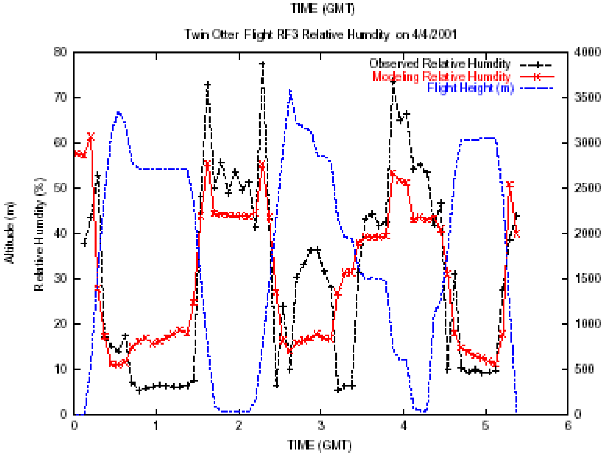




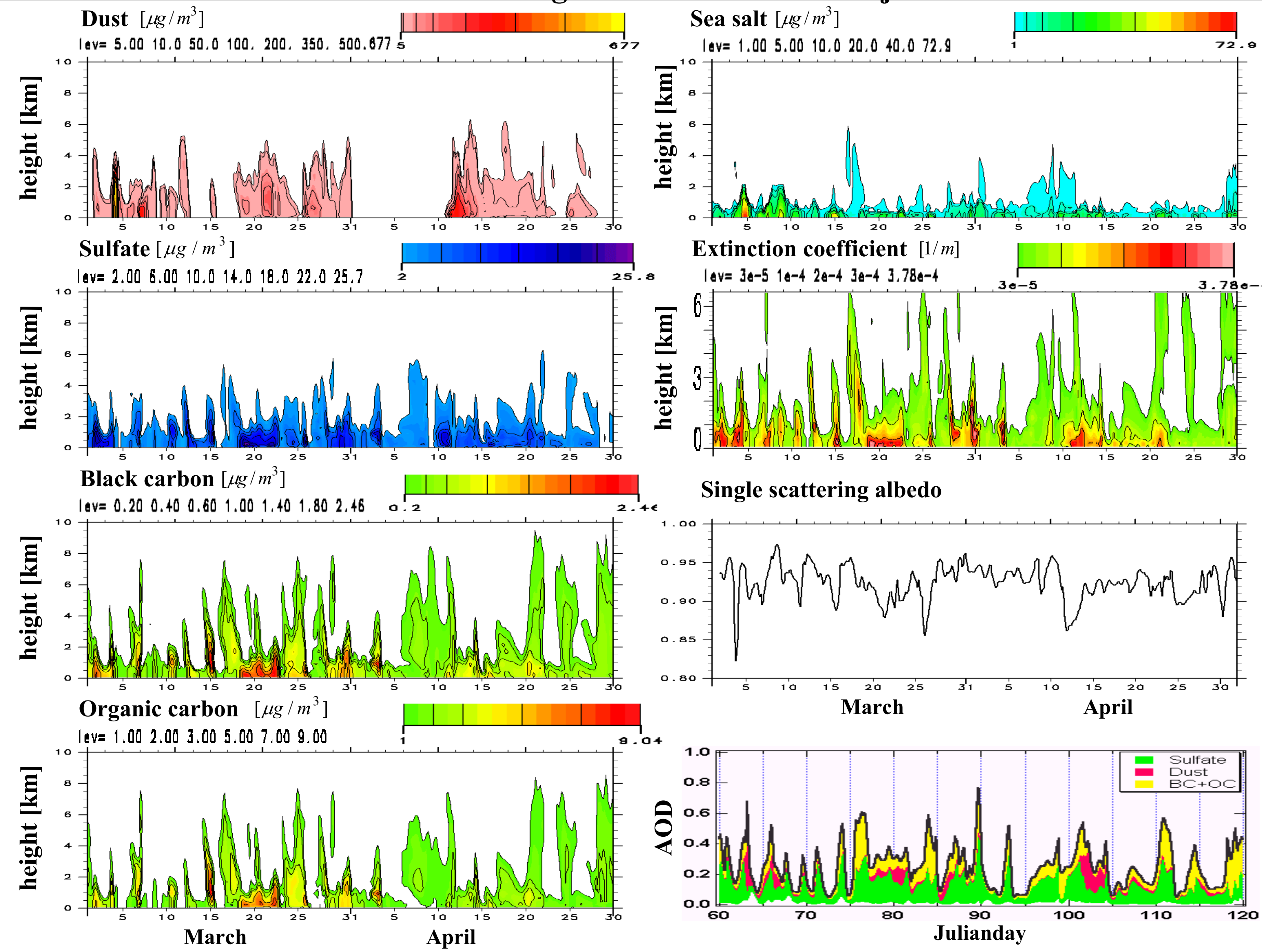




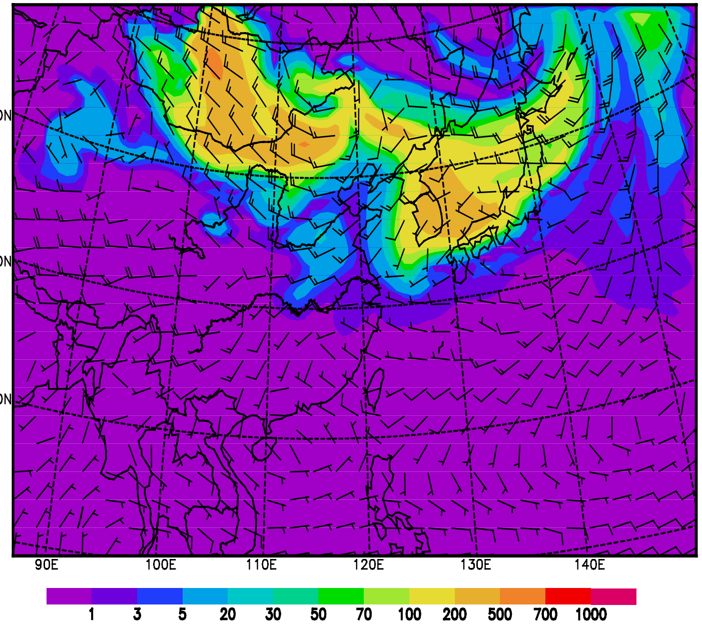




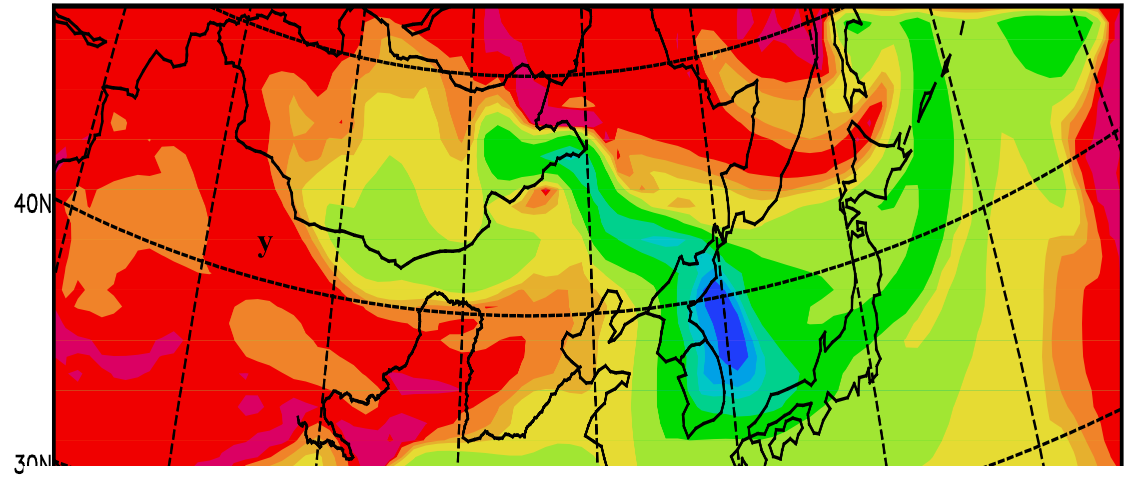
Time-height cross section at Cheju



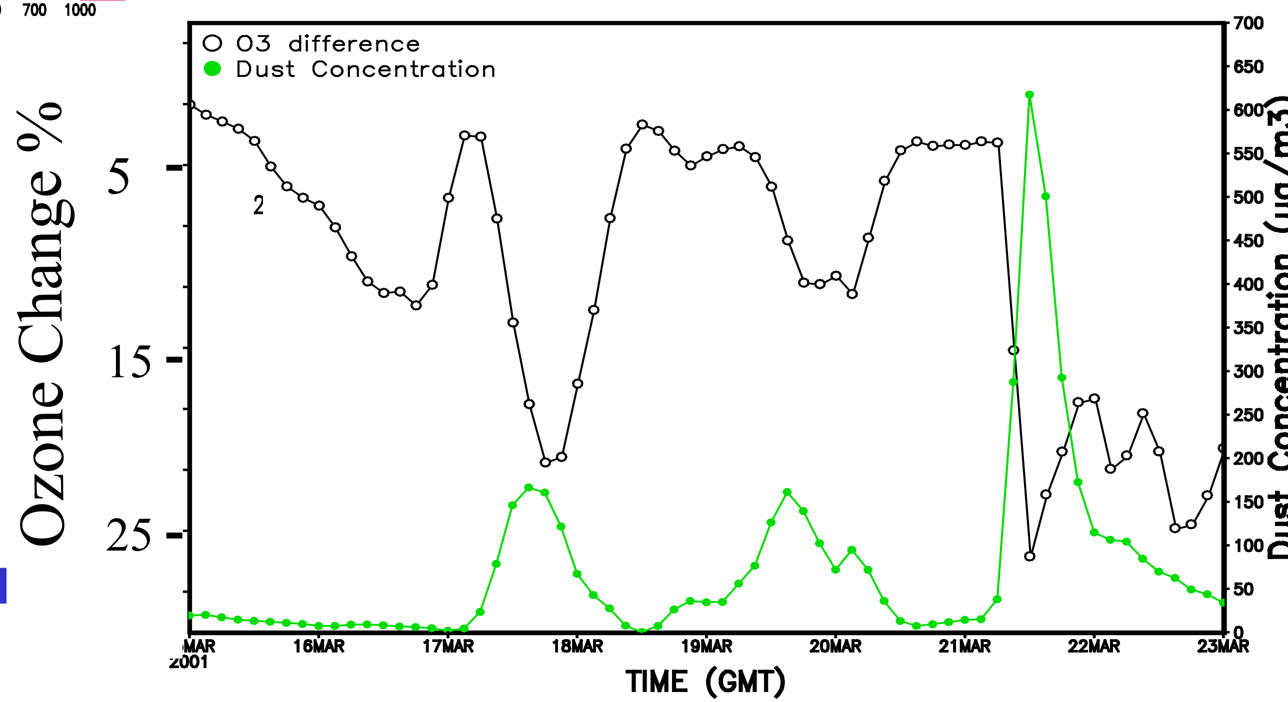
Simulated Dust Concentration (ug/m3) in the 1km layer at 03GMT, 03/21/2001

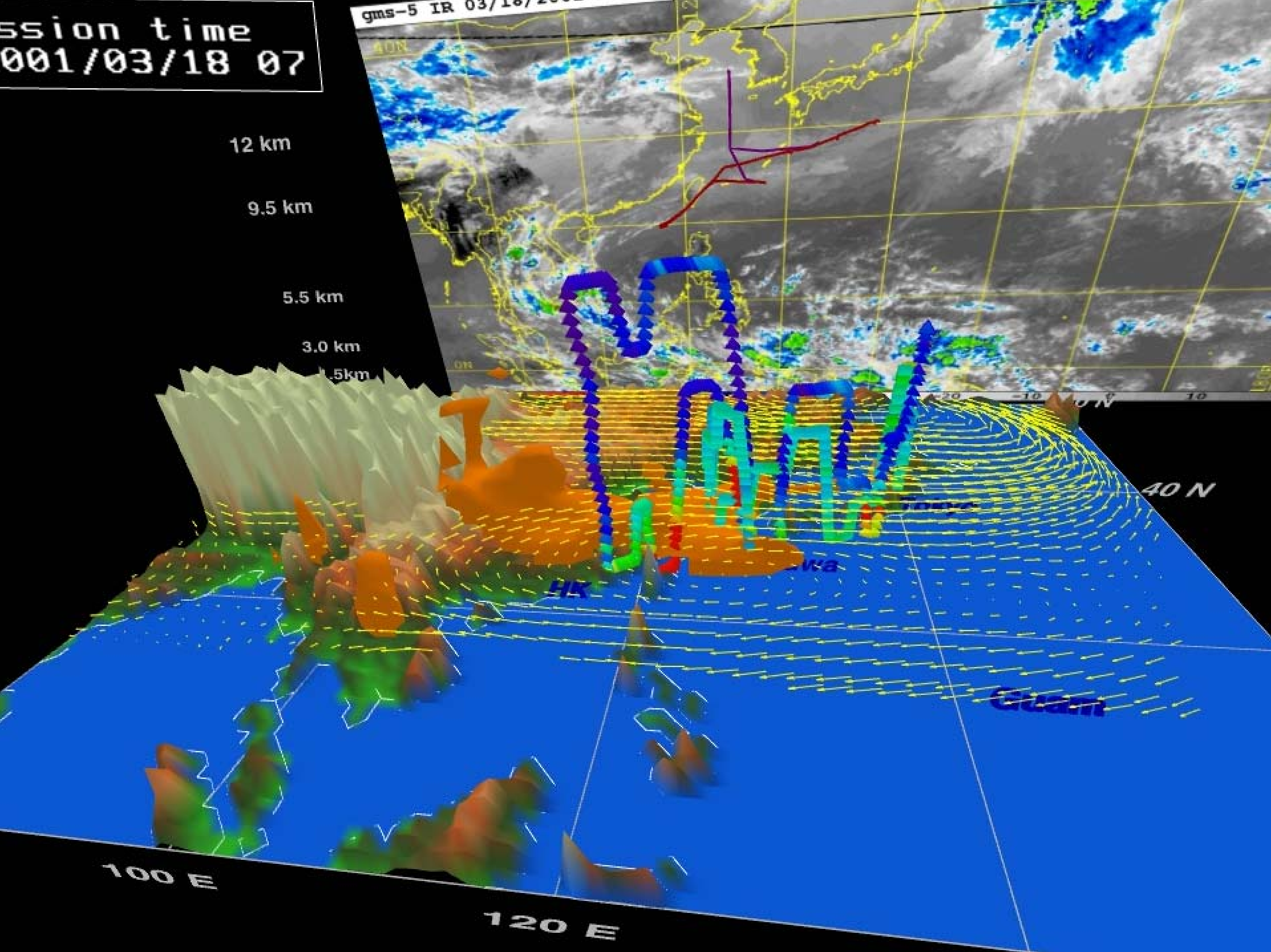


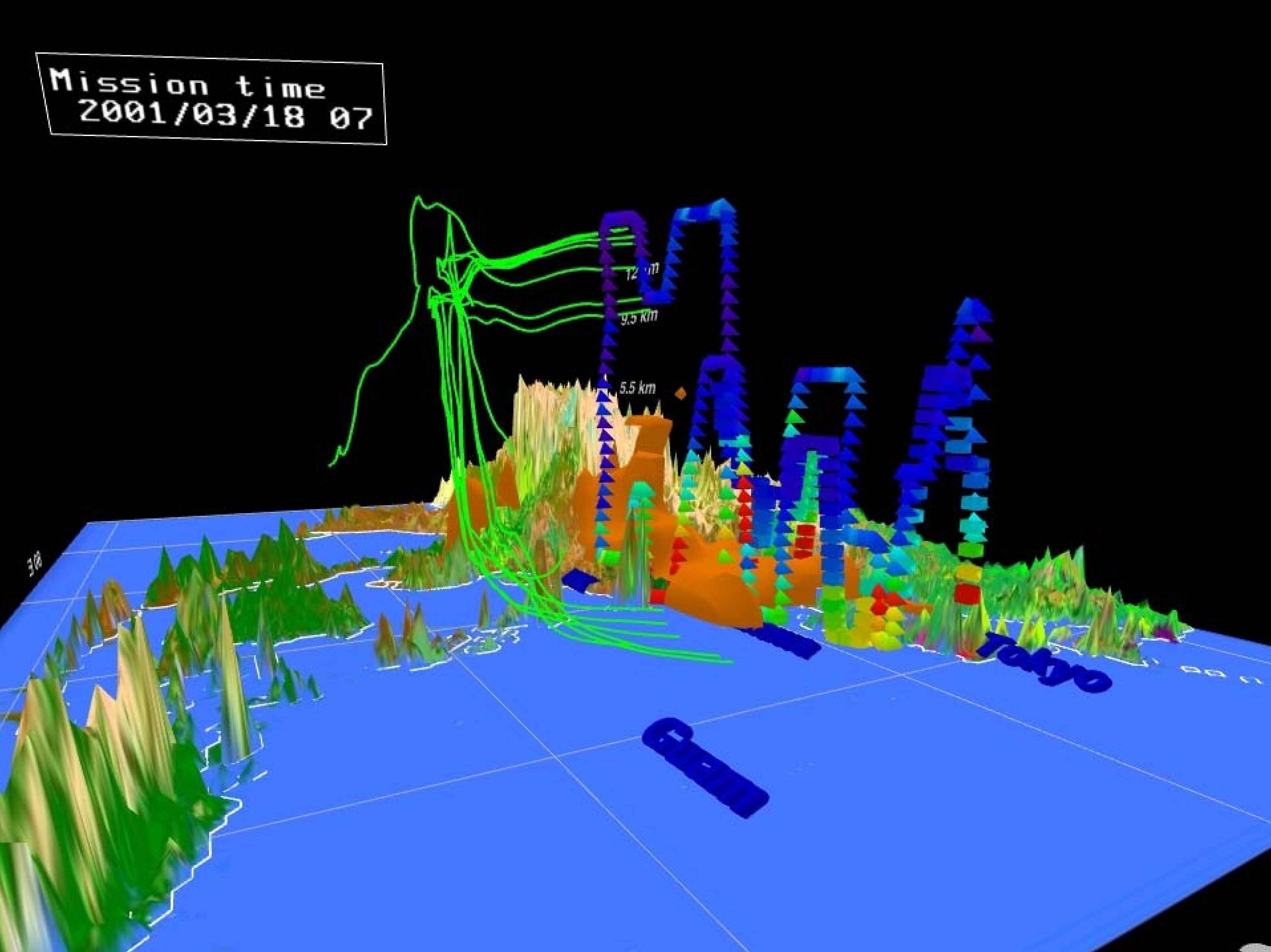
O3 Concentration Change (ppbv) after Considering Heterogeneous Reactions in the 1km layer at 03GMT, 03/21/2001



O3 Concentration difference between the cases with and without heterogeneous reactions, over surface laer of Beijing

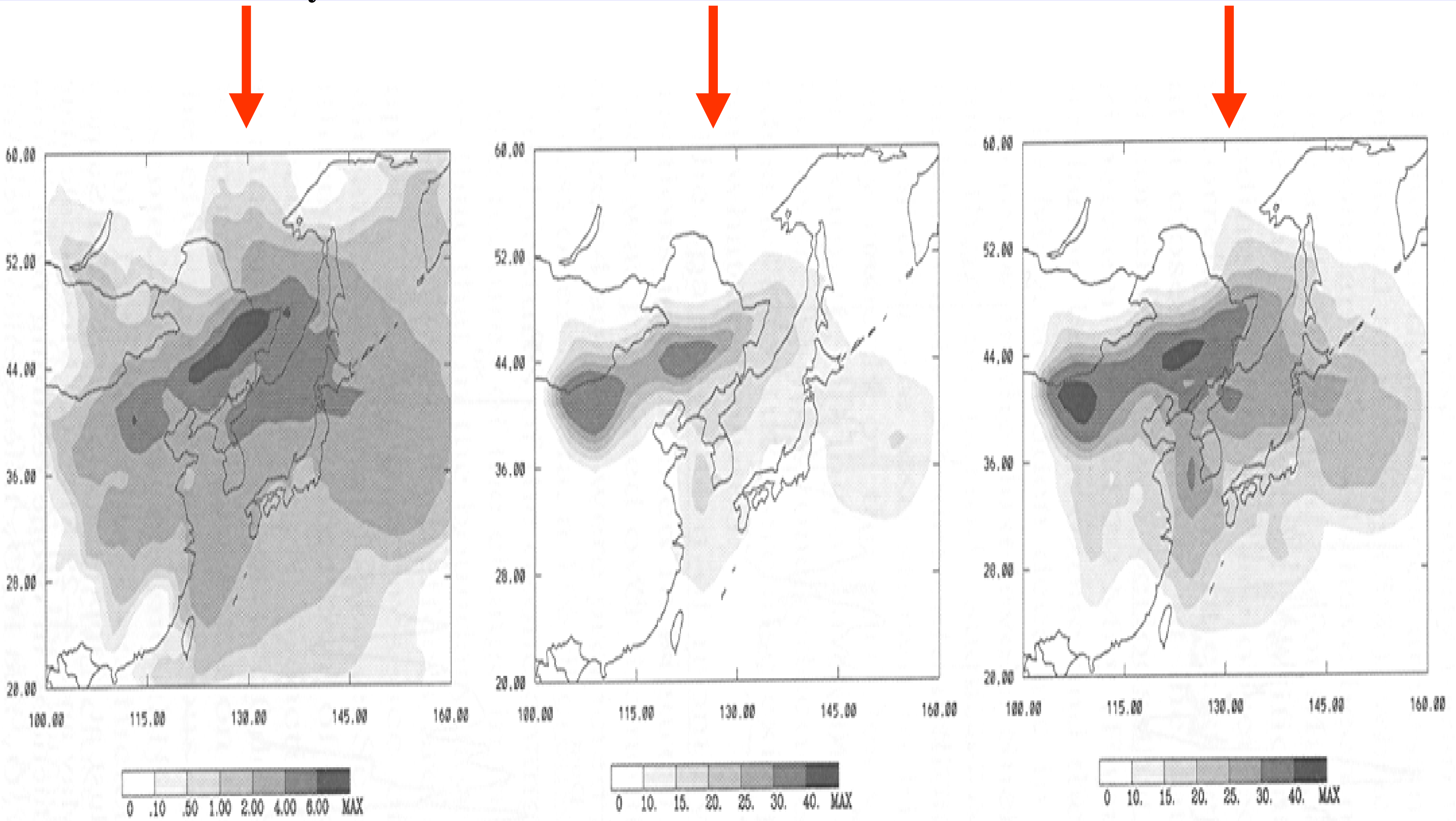



ssion time
001/03/18 07
12 km
9.5 km
5.5 km
3.0 km
40 N
HK
Guam
100 E
120 E


Mission time
2001/03/18 07
9.5 km
5.5 km
Tokyo

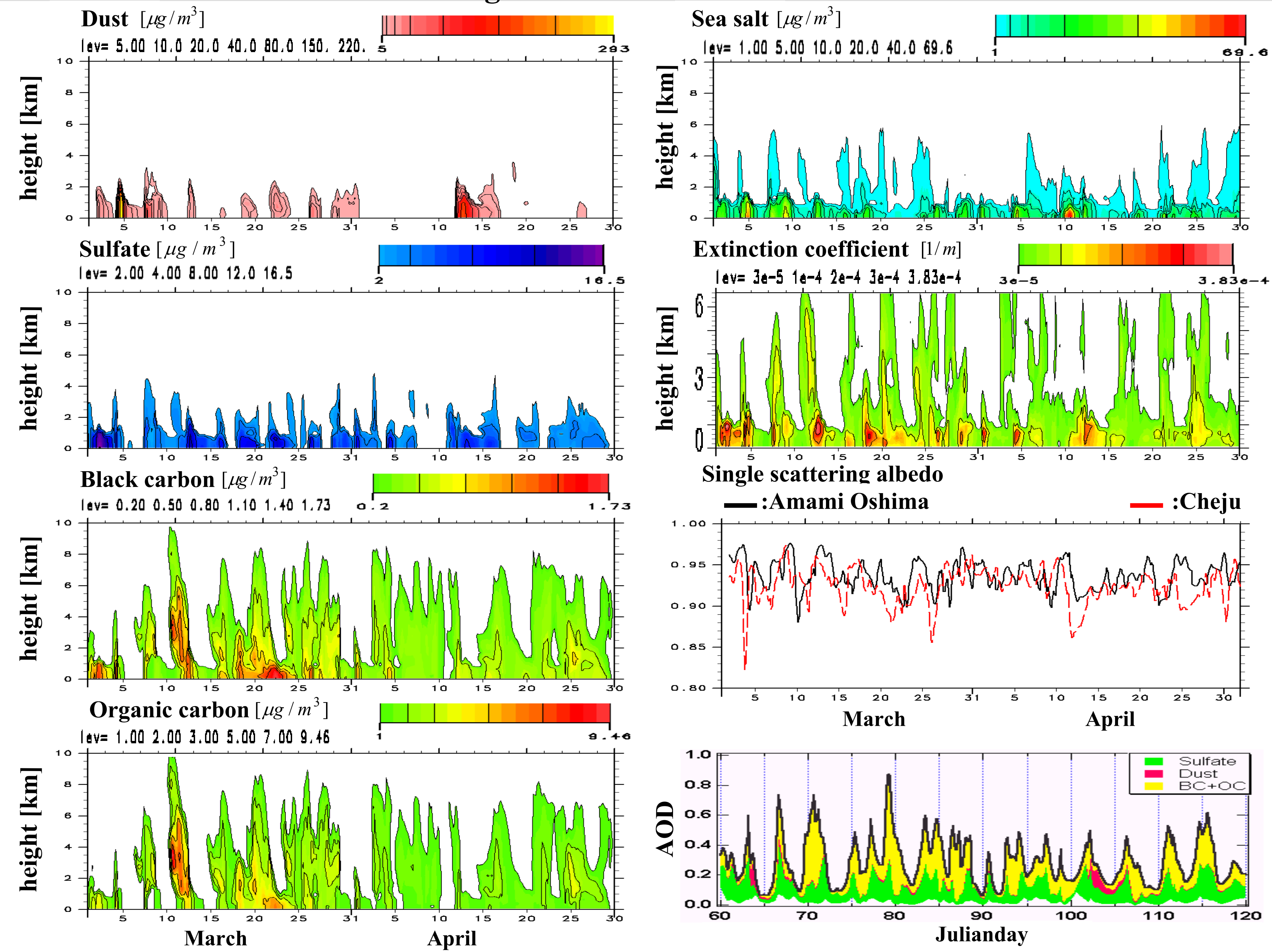
% Change in O_3 in May 1987 due to:

NO_x + H_xO_y Rxns; Direct O_3 Rxn; and Combination

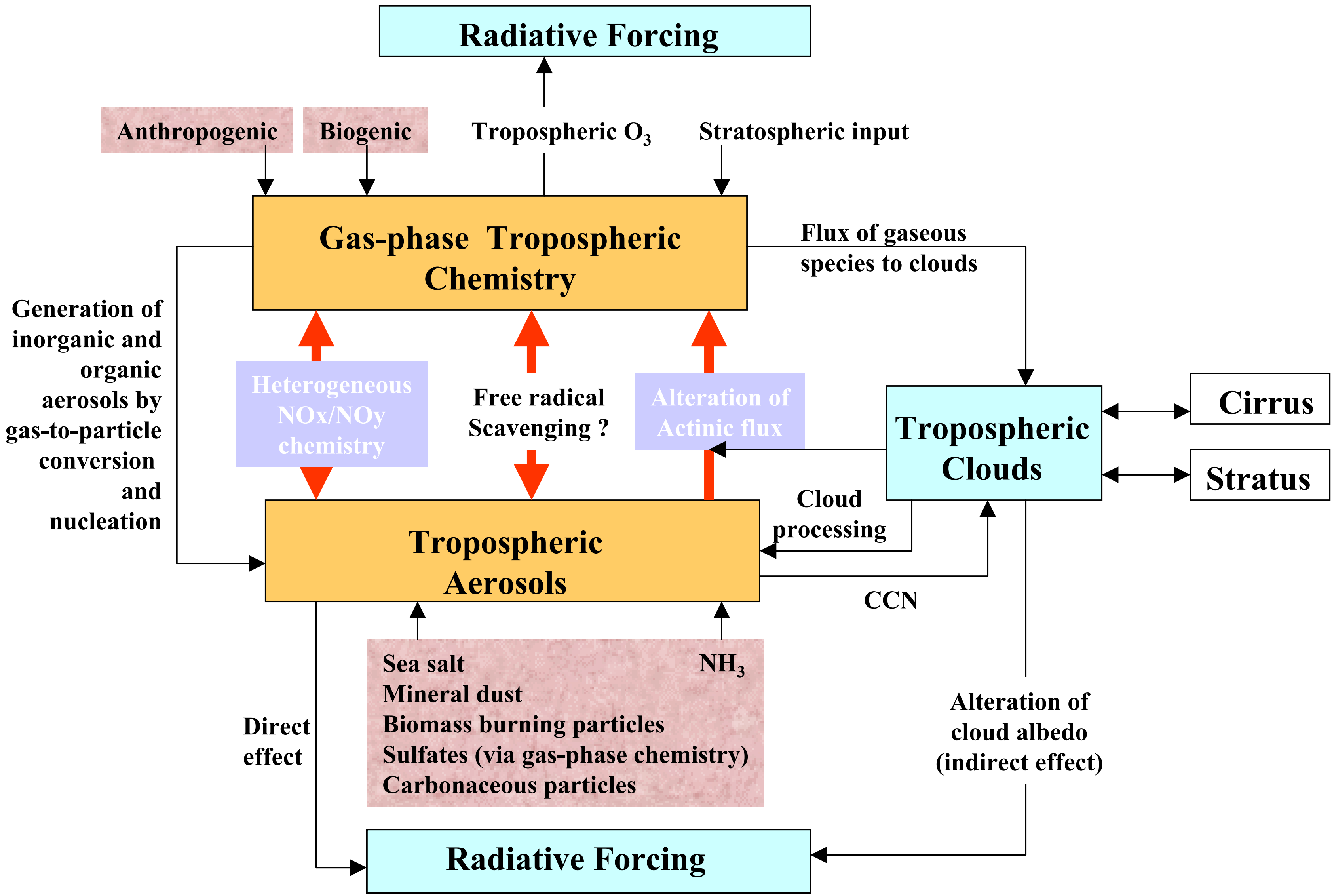


Phadnis et al., J. Atmos. Chem., 40: 1-22 (2001)

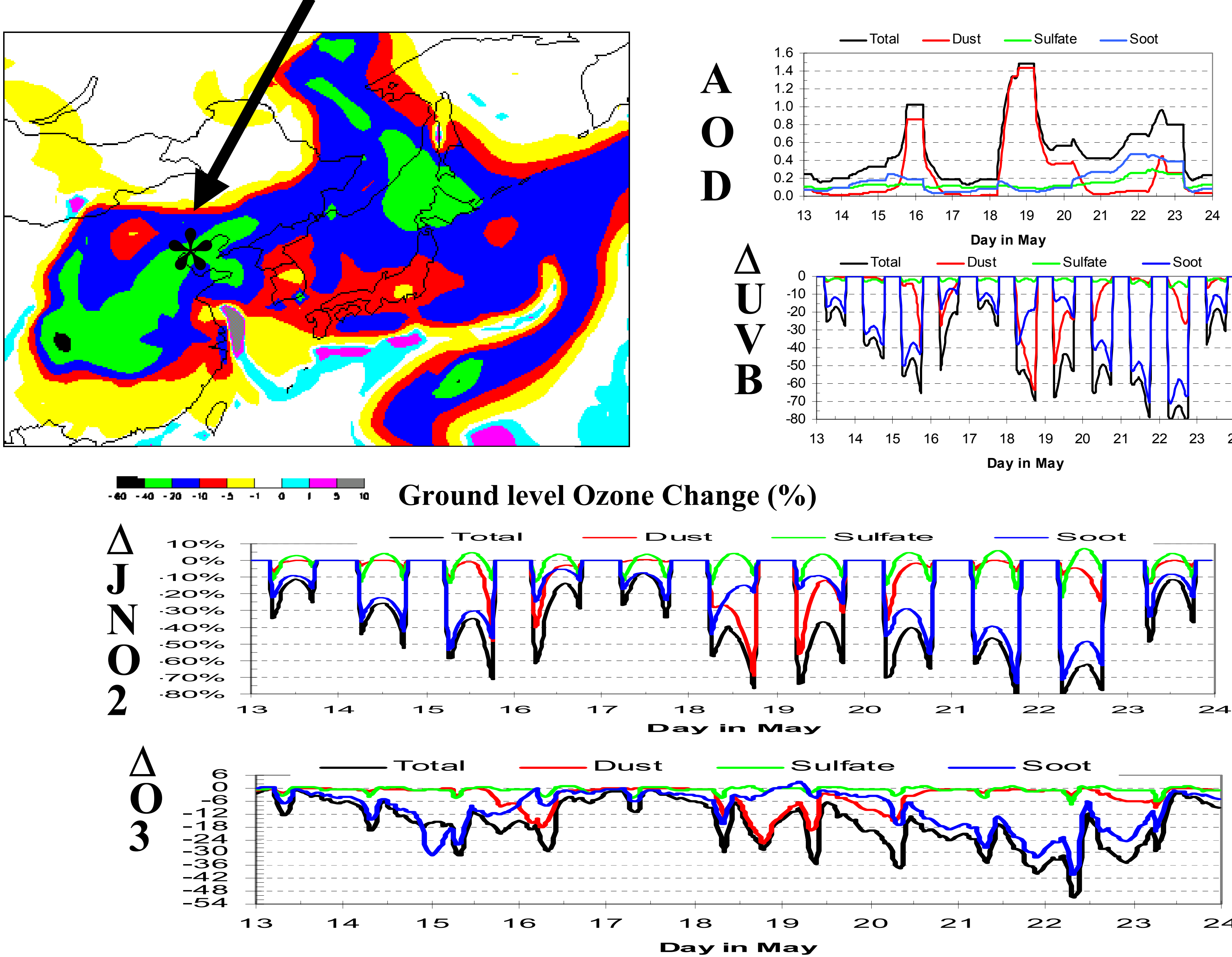
Time-height cross section at Amami Oshima



A Key Science Issue: A Better Understanding of Chemistry/Aerosol Interactions

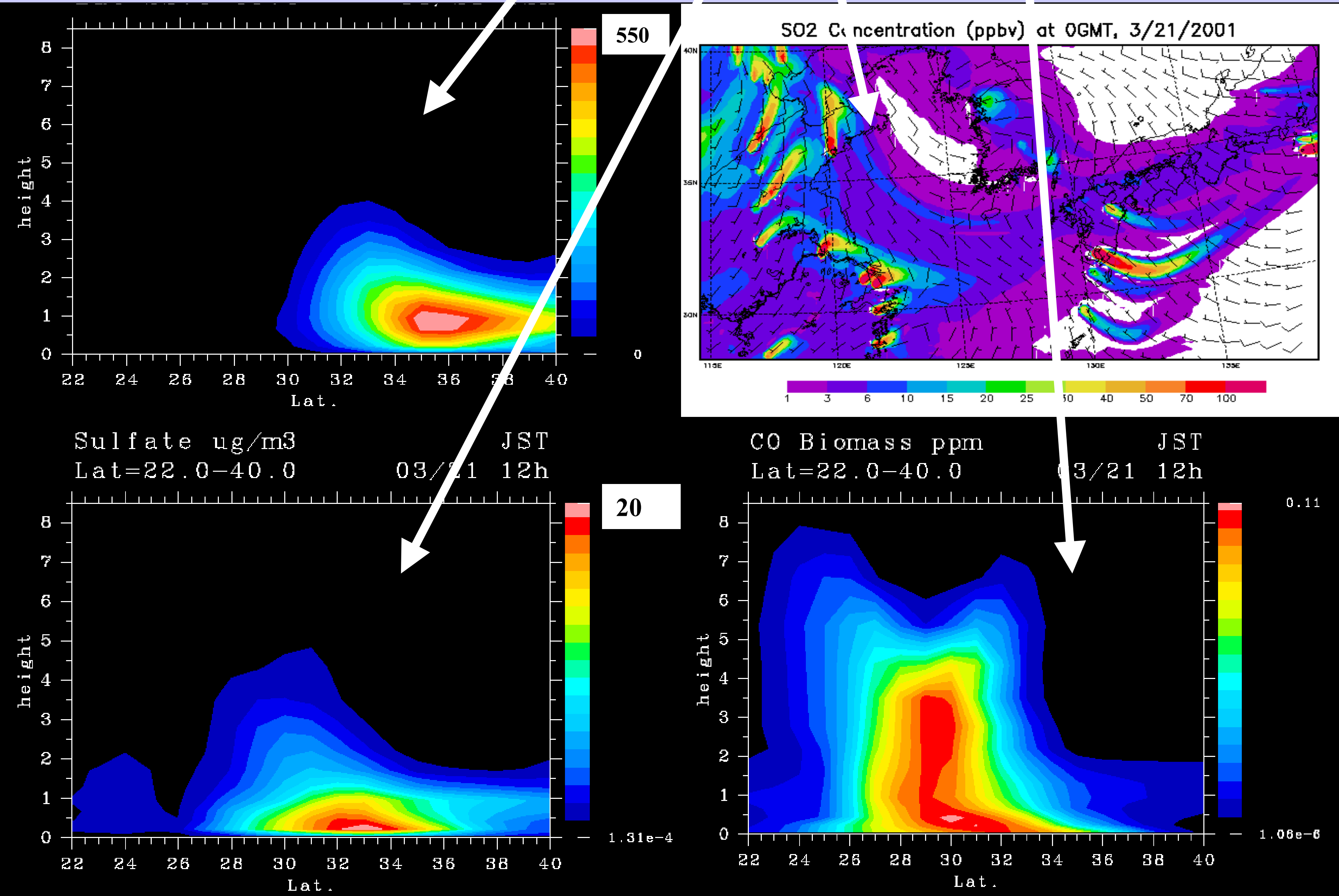


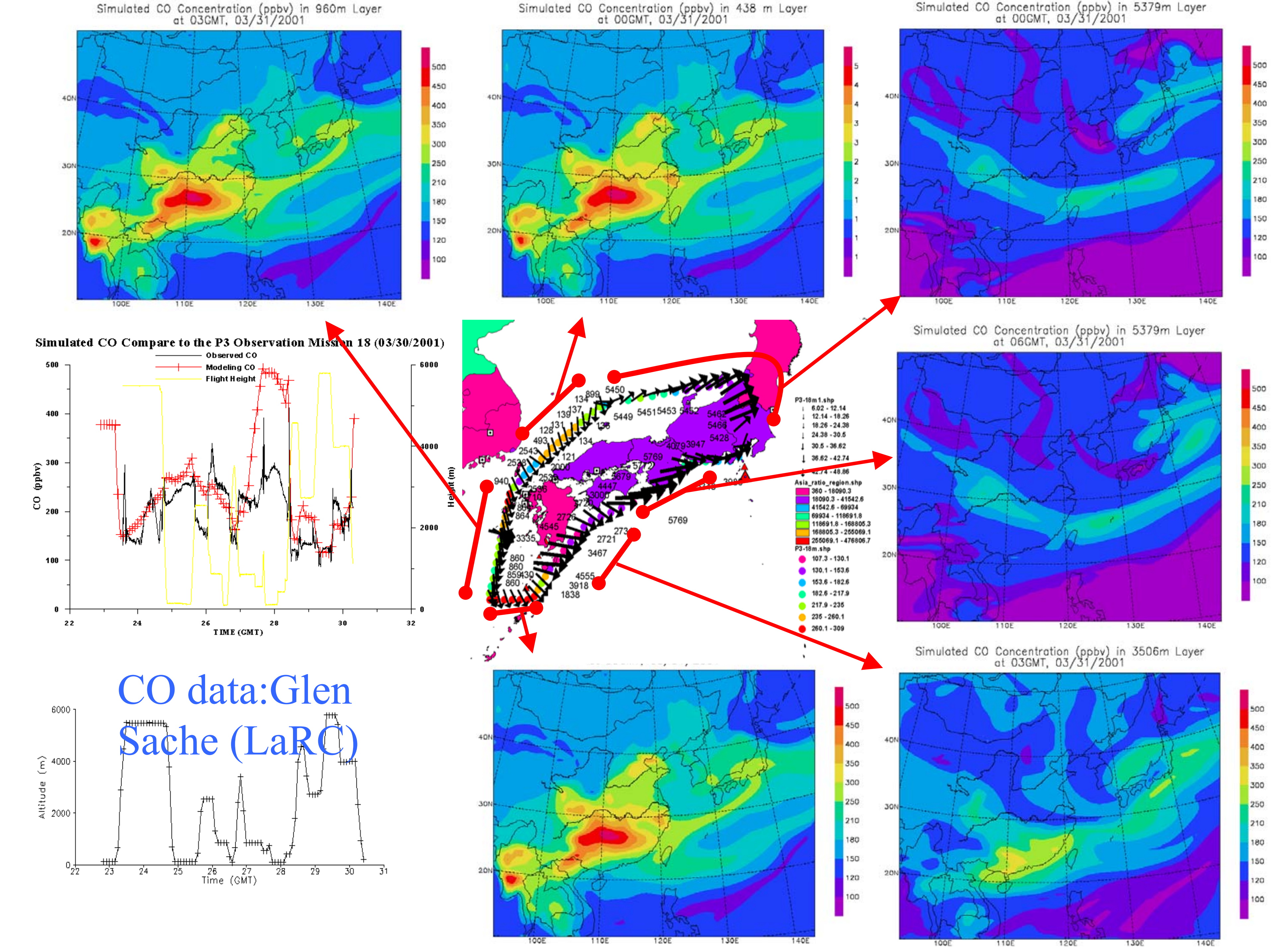
modified after J.H.Seinfeld 1999

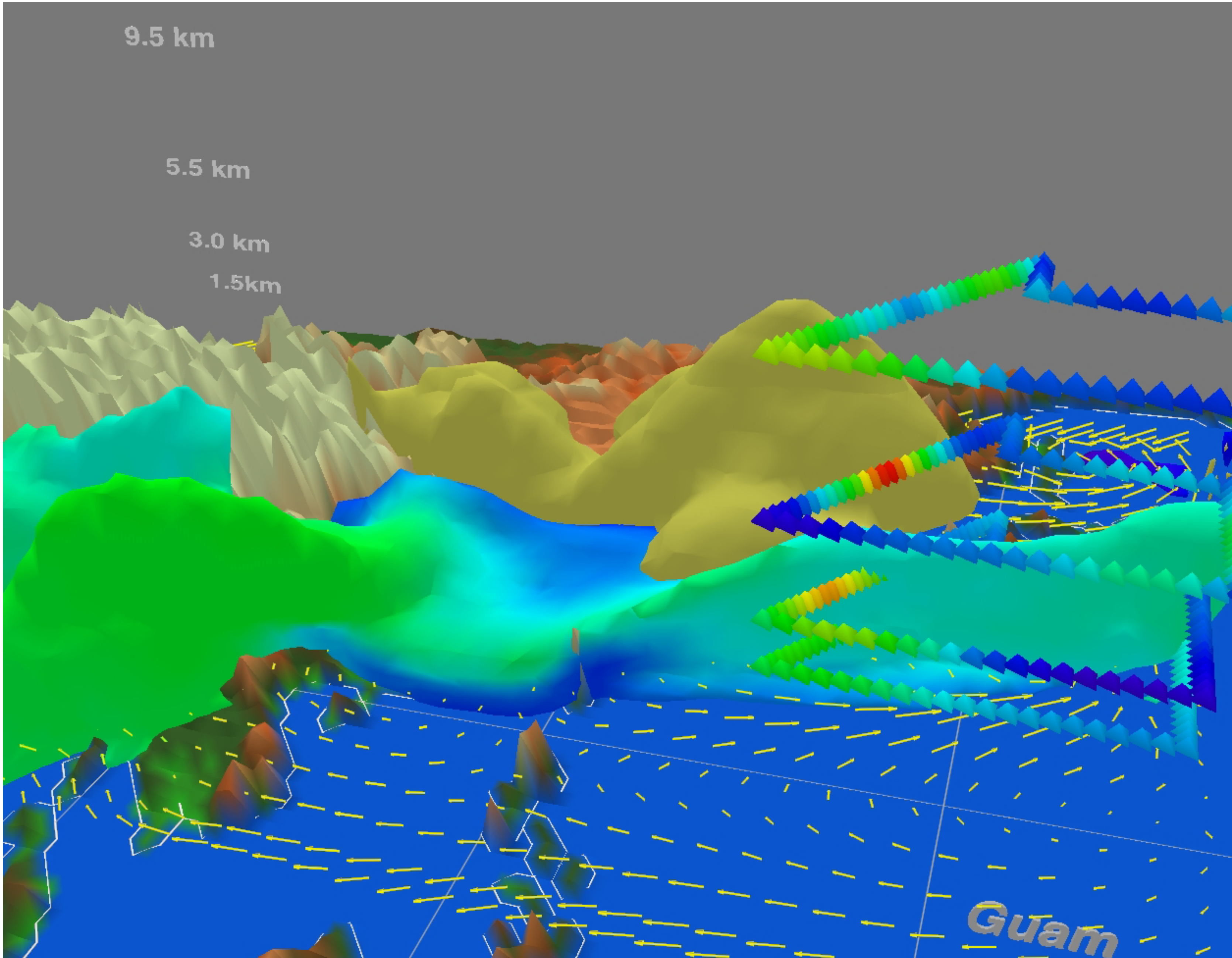


Ground level Ozone Change (%)
-60 -40 -20 -10 -5 -1 0 1 5 10
AOD
Total
Dust
Sulfate
Soot
Day in May
ΔUVB
Total
Dust
Sulfate
Soot
Day in May
ΔJNO2
Total
Dust
Sulfate
Soot
Day in May
ΔO3
Total
Dust
Sulfate
Soot
Day in May

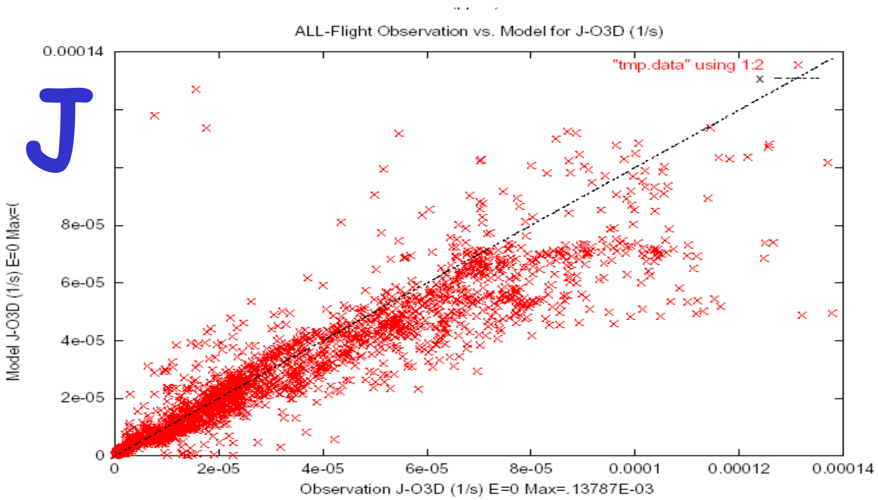
125 E Dust; SO4; SO2; CO-biom



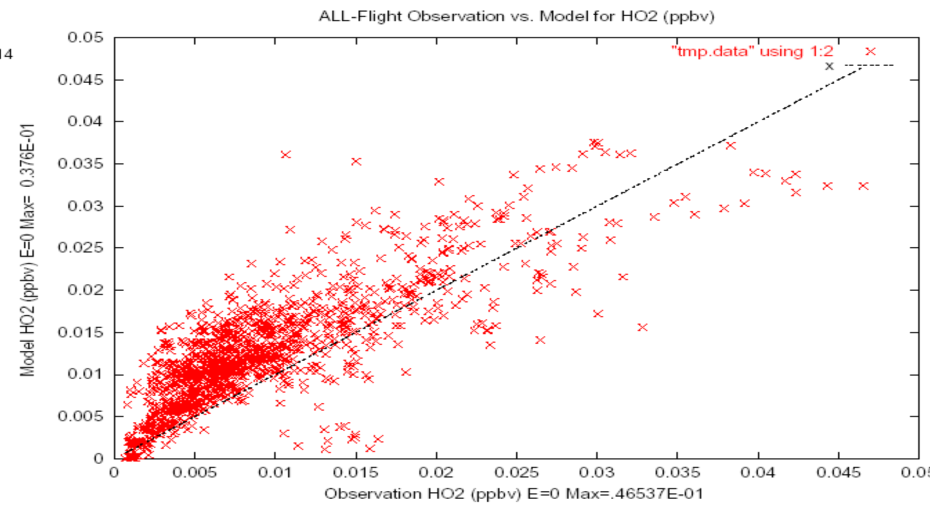

Simulated CO Concentration (ppbv) in 960m Layer at 03GMT, 03/31/2001
Simulated CO Concentration (ppbv) in 438 m Layer at 00GMT, 03/31/2001
Simulated CO Concentration (ppbv) in 5379m Layer at 00GMT, 03/31/2001
Simulated CO Compare to the P3 Observation Mission 18 (03/30/2001)
Observed CO
Modeling CO
Flight Height
CO (ppbv)
Height (m)
TIME (GMT)
Simulated CO Concentration (ppbv) in 5379m Layer at 06GMT, 03/31/2001
Simulated CO Concentration (ppbv) in 3506m Layer at 03GMT, 03/31/2001
CO data:Glen Sache (LaRC)
Altitude (m)
Time (GMT)
P3-18m1.shp
Asia_ratio_region.shp
P3-18m.shp

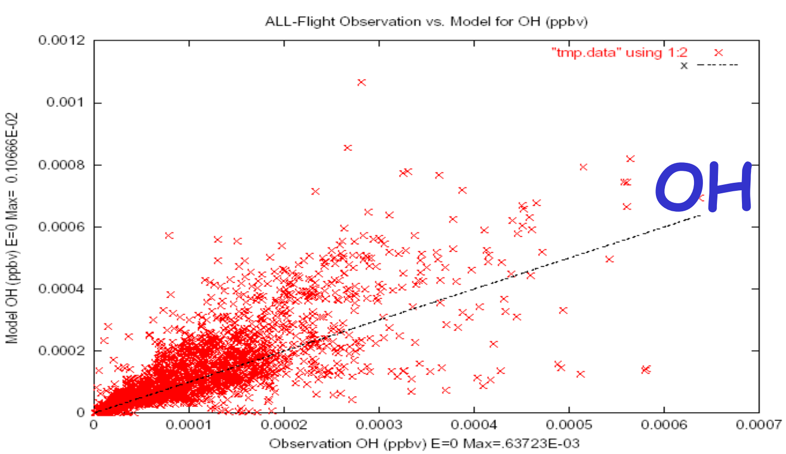

9.5 km
5.5 km
3.0 km
1.5km
Guam

J's OH & HO2



HO2

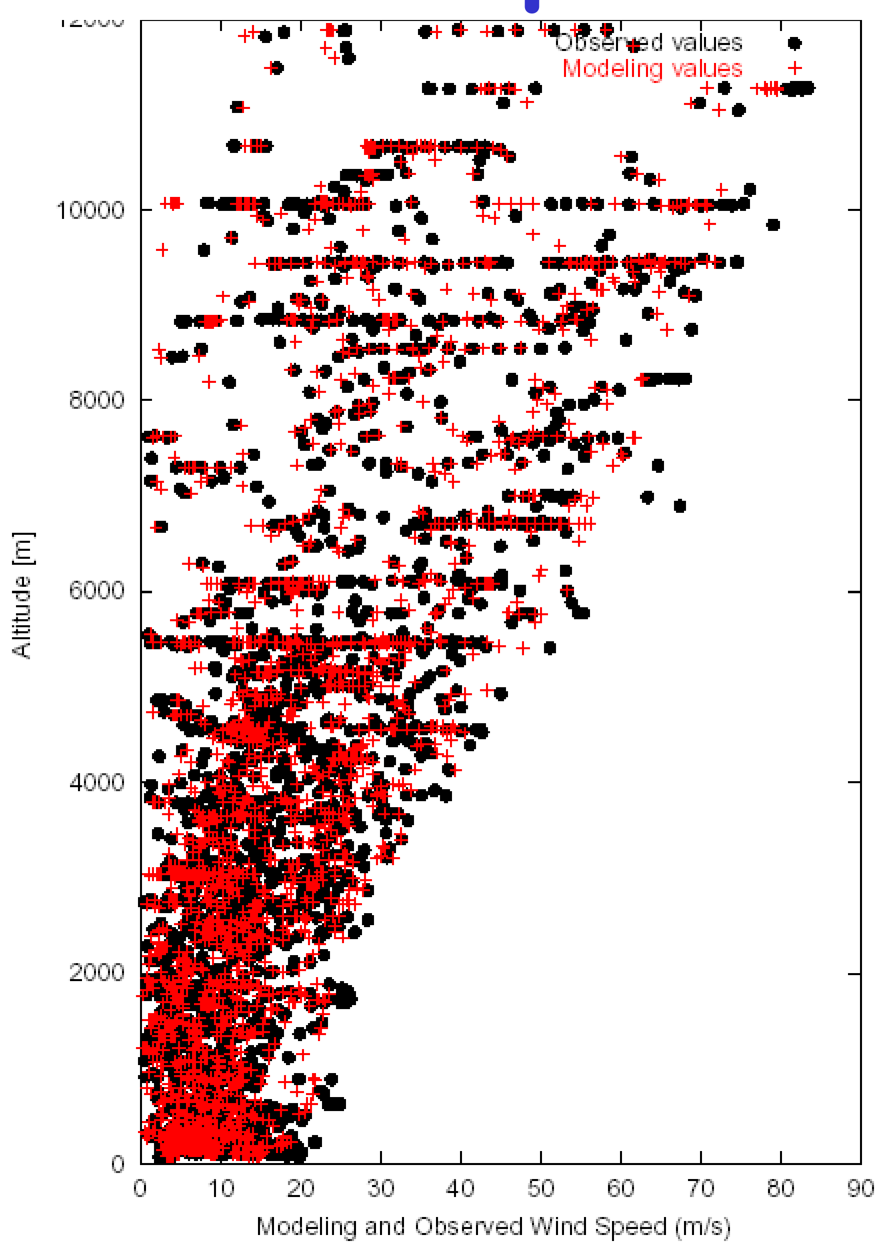




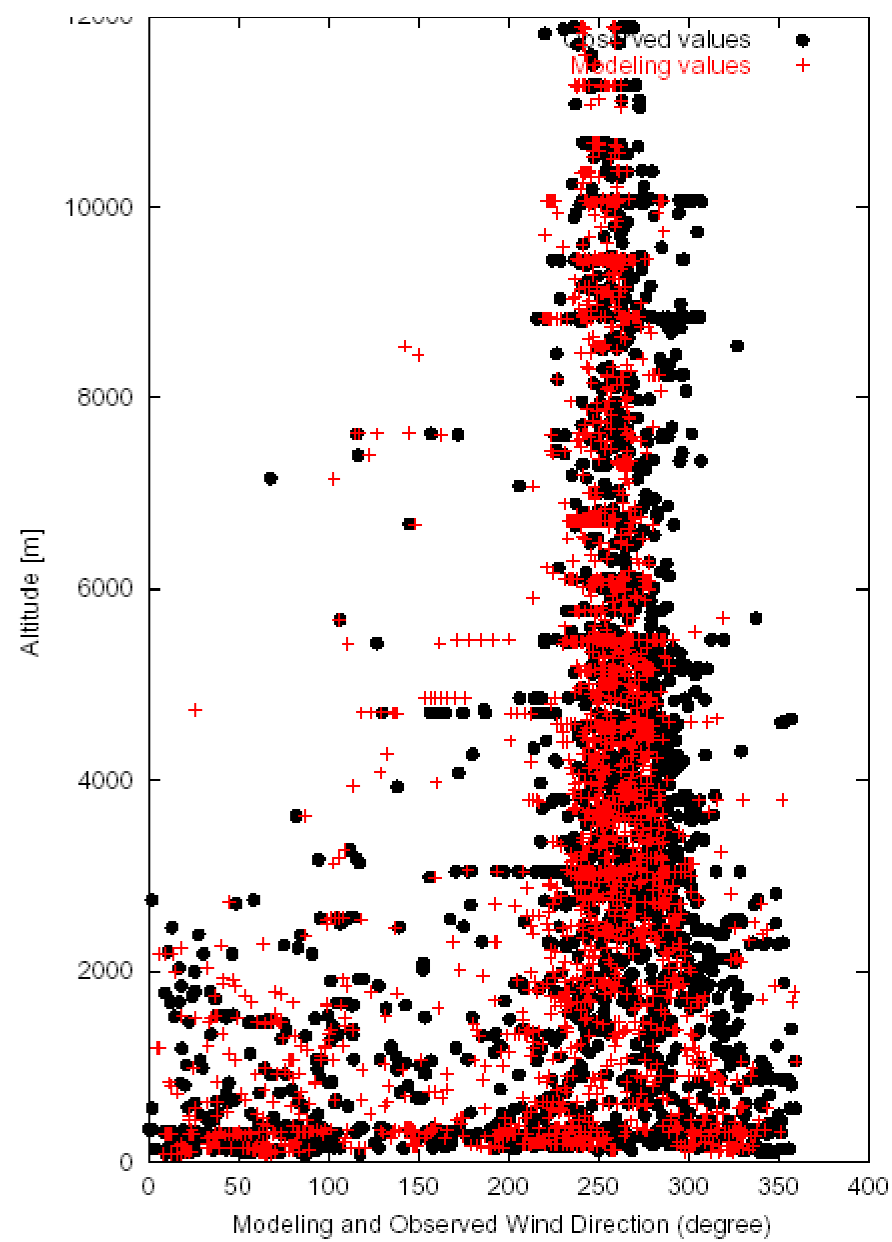
Photolysis data: Shetter (NCAR)

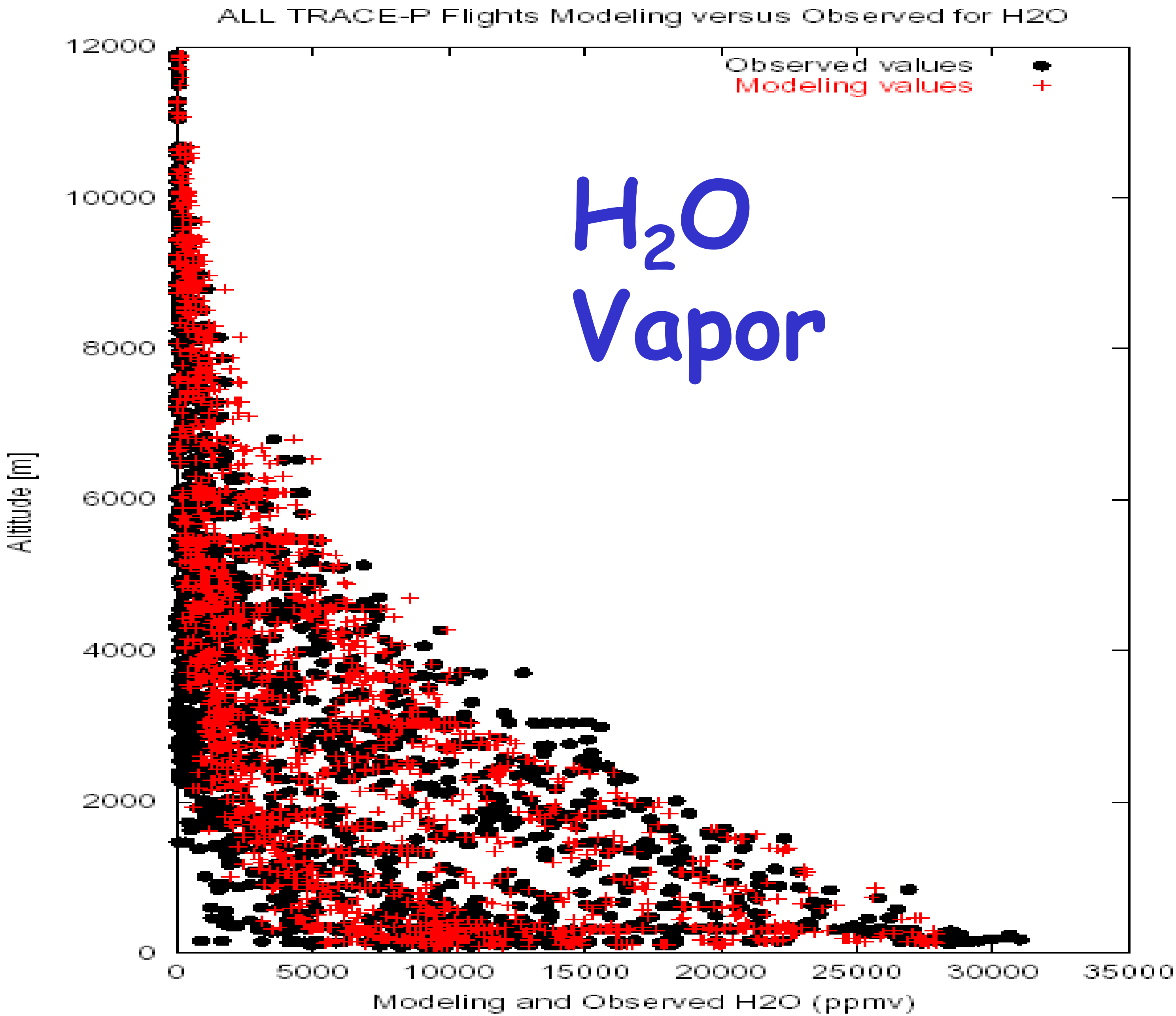
OH/HO2: Brune (Penn St.) and Contrell (NCAR)

Wind Speed

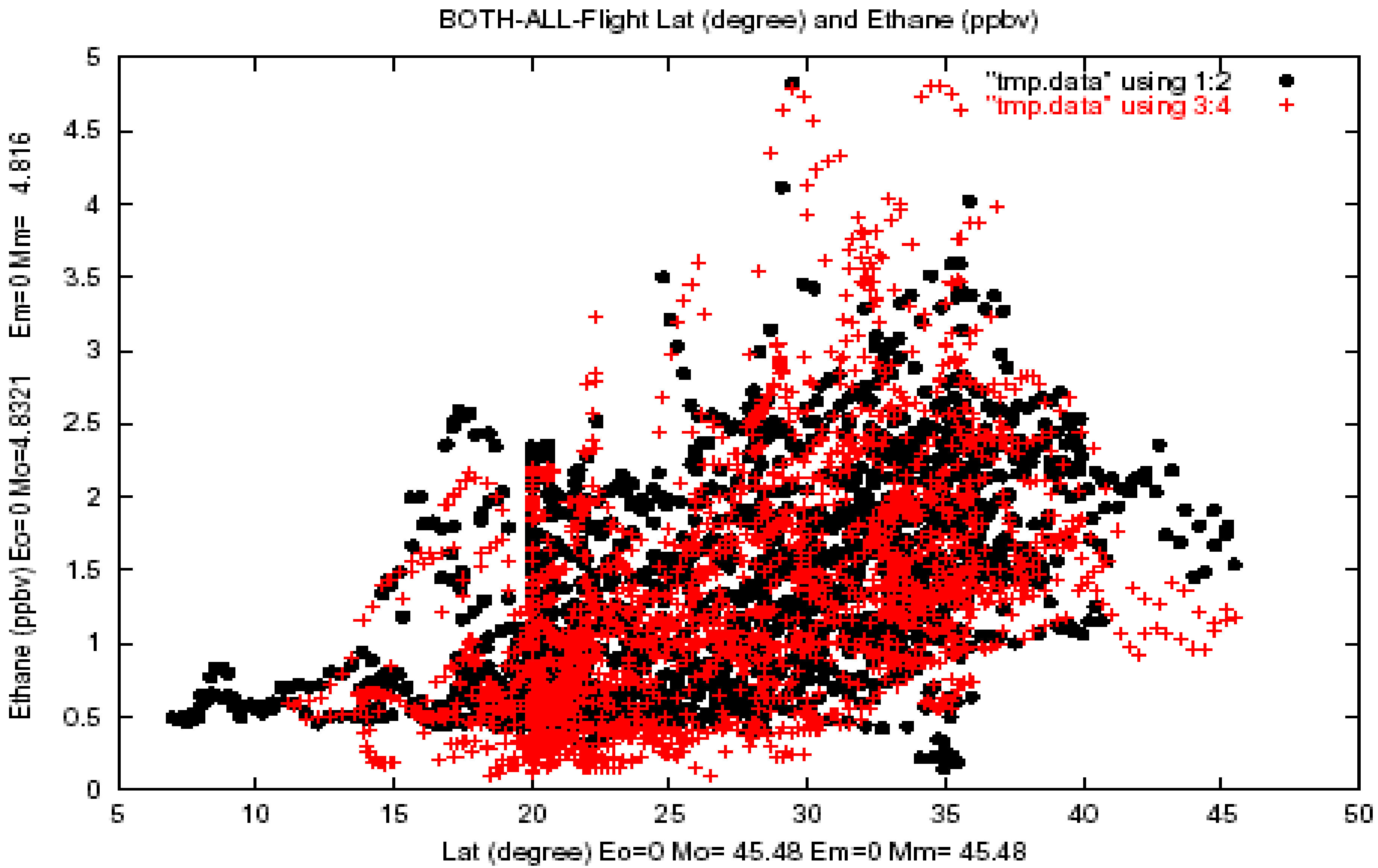


Wind Direction




ALL TRACE-P Flights Modeling versus Observed for H2O
Observed values
Modeling values
H2O Vapor
Altitude [m]
12000
10000
8000
6000
4000
2000
0
0
5000
10000
15000
20000
25000
30000
35000
Modeling and Observed H2O (ppmv)

Measured and Modeled Ethane (Blake et al.) as a Function of Latitude DC8 & P3 Flights



Measured and Modeled Ozone (Melody Avery) as a Function of Latitude DC8 & P3 Flights